Characterisation of Nano-structured Coatings Containing Aluminium, Aluminium-Nitride and Carbon

A thesis submitted for the degree of Doctor of Philosophy

by

Xiaoling XIAO

School of Applied Science (Applied Physics)
Science, Engineering and Technology Portfolio
RMIT University.
Australia.
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To my family
Declaration

The Ti/TiN multilayer sample presented in Chapter 2 section 2.2.3.1 was prepared and the nanohardness measured by Luke Ryves of The University of Sydney. The amorphous Carbon multilayer presented in Chapter 4 section 4.1 was made by Dr. Peter C.T. Ha of The University of Sydney. With these exceptions, this thesis contains no materials which have been presented for a degree at any other university. To the best of my knowledge and belief, it contains no copy or paraphrase of work published by other people, except where duly acknowledged in the text.

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   X. L. Xiao, D. G. McCulloch, S. H. N. Lim, A. R. Merchant


Abstract

There is an every increasing need to develop more durable and higher performing coatings with superior properties for use in a range of products including tools, devices and bio-implants. Nano-structured coatings either in the form of a nanocomposite or a multilayer is of considerable interest since they often exhibit outstanding properties. The objective of this thesis was to use advanced plasma synthesis methods to produce novel nano-structured coatings with enhanced properties. Coatings consisting of combinations of aluminum (Al), aluminum nitride (AlN) and amorphous carbon (a-C) were investigated. Cathodic vacuum arc deposition and unbalanced magnetron sputtering were used to prepare the coatings. By varying the deposition conditions such as substrate bias and temperature, coatings with a variety of microstructures were formed.

A comprehensive range of analytical methods have been employed to investigate the stoichiometry and microstructure of the coatings. These include Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM), Electron Energy Loss Spectroscopy, Auger Electron Spectroscopy, X-ray diffraction and Raman spectroscopy. In addition to the investigation of microstructure, the physical properties of the coatings were measured. Residual stress has been recognized as an important property in the study of thin film coatings since it can greatly affect the quality of the coatings. For this reason, residual stress has been extensively studied here. Hardness measurements were performed using a nano indentation system, which is sensitive to the mechanical properties of thin films.

This thesis undertook the most comprehensive investigation of the Al/AlN multilayer system. A major finding was the identification of the conditions under which layers or nanocomposite form in this system. A model was developed based on energetics and diffusion limited aggregation that is consistent with the experimental data. Multilayers of a-C and Al were also found to form nanocomposites. No hardness enhancement as a function of layer
thickness or feature size was observed in either the Al/AlN or a-C/a-C systems. It was found that the most important factor which determines hardness is the intrinsic stress, with films of high compressive stress exhibiting the highest hardness.

Nano-structured multilayers of alternating high and low density a-C were investigated. For a-C multilayers prepared using two levels of DC bias, evidence of ion beam induced damage was observed at the interfaces of both the low and high density layers. In addition, the structure of the high density (ta-C, known as tetrahedral amorphous carbon) layers was found to be largely unchanged by annealing. These results extend our understanding of how a-C form from energetic ion beams and confirms the thermal stability of ta-C in a multilayer. This thesis also presented the first attempt to synthesis a-C multilayered films with a continuously varying DC bias in sinusoidal pattern. The resulting films were shown to have a structurally graded interface between layers and verified that ion energy and stress are the most important factors which determine the structure of a-C films.
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Chapter 1

Introduction

1.1 Surface Treatments and Coatings

Wear and corrosion are the main causes of direct and indirect engineering component failure which costs the economy many millions of dollars per year. This failure often occurs at the surface of a component. Surface treatments can be used to enhance the properties of materials and improve their performance when used in engineering components. Surface treatments include traditional methods such as painting, electroplating, nitriding and carburising, as well as newer technologies such as laser surfacing, ion implantation and the physical and chemical vapour deposition of coatings. Of particular interest are new coating technologies to improve the performance of tools and components for use in demanding applications within the automotive and aerospace industries.

Nano-structured coatings have received considerable attention in recent years with many authors reporting that these types of coatings exhibit enhanced properties [1-4]. There are two kinds of nano-structured coatings: nano-structured multilayer coatings and nanocomposite coatings. Nano-structured multilayer coatings are composed of a periodic structure with layers of two or more materials with thicknesses on the nanometer scale [1]. A schematic of a multilayer coating comprised of two types of materials with a period, $\lambda$ (or bilayer thickness, defined as being the thickness of two adjacent layers), is shown in figure 1.1(a). Nanocomposite coatings are composed of at least two phases which are mutually immiscible and form very fine dispersions of one phase within the second phase [4] (as shown in figure 1.1(b)).
Nature provides a dramatic example of multilayer structure in the form of an abalone shell, which is an incredibly tough (resistance to breakage), and is made up of alternating layers of one soft (biological macromolecule, approximately 20nm) and one brittle material (aragonite, approximately 500nm) \[5\]. Therefore the prospect of fabricating nano-structured materials with enhanced properties for practical applications is considered plausible.

Recent studies have demonstrated that superior properties such as superhardness ($\geq 40\text{GPa}$), wear resistance and corrosion resistance can be achieved by a nano-structured multilayer design [1-4, 6-10]. This makes nano-structured multilayered systems potentially attractive for a variety of demanding applications. For example, a cutting tool coating, with high hardness and toughness, and capable of operation at high temperature without requiring lubrication. This would eliminate the adverse environmental impacts of oil-based lubricants required for high speed cutting applications with conventional tooling. High-toughness coatings are also needed for industrial sensors operating in harsh environments and for the next generation of biomedical devices and prostheses. Other properties such as oxidation resistance, roughness and reflectivity play very important roles in their application in optics, optical magnetic storage and microelectronics. It is a scientific challenge to be able to control the structure and composition of coatings at the nanoscale so that their properties can be tailored for a particular industrial application.
1.2 Objectives and Aims

In order to understand the microstructural factors and physical mechanisms responsible for enhanced properties seen in nano-structured coatings, this thesis will combine experimental synthesis with microstructural analysis. The aim of this project is to characterize several types of nano-structured coatings in order to understand how the physical aspects of a coating (feature size, composition etc.) affect the coatings’ properties.

Another area of interest in nano-structured multilayer coatings is the nature of the interface between layers and how this affects its properties. Two types of interfaces: a sharp interface and a graded interface (shown in figure 1.2) will be fabricated. The latter type of interface can be formed by combining film deposition with ion bombardment. This thesis will explore whether it is possible to create gradient interfaces and develop ways of reliably producing these different interface types and determine their impact on macroscopic properties, such as indentation hardness and stress, in systems with a range of microstructures.

![Figure 1.2 Schematic diagrams showing two distinct types of interfaces: (a) sharp, (b) graded.](image)

The specific aims are to:

1. Synthesise nano-structured coatings of Aluminium/Aluminium Nitride, high/low density amorphous carbon (a-C) and Aluminium/a-C using physical vapour deposition techniques.
2. Investigate the microstructure of these coatings and relate these findings to the particular deposition parameters employed so that the optimum conditions for coatings formation can be identified.

3. Evaluate the mechanical properties of the coatings, particularly the intrinsic stress, hardness and elastic modulus.

4. Determine whether there is a link between microstructure and mechanical properties so that coatings can be synthesised with enhanced properties.

5. Investigate whether the interfaces between layers in a multilayer can be graded by combining film deposition with ion implantation. Determine the nature of any interface structures.

Major outcomes of this work include:

1. The most thorough investigation of the Al/AlN nano-structured coatings system including the identification of conditions which give rise to multilayers and those which produce nanocomposites.

2. A detailed analysis of multilayer carbon coatings both with sharp and graded interfaces including the first study of the formation of a multilayer by continuously varying the ion energy in sinusoidal pattern during growth. These samples are used to determine whether the film stress is the most important factor determining the microstructure of amorphous carbon in multilayers.

3. The demonstration that high spatial resolution analysis is required to fully understand the microstructure of nano-structured coatings and to identify unforeseen changes in microstructure and composition.

1.3 Thesis Outline

Chapter 2 outlines the theories associated with the enhanced mechanical properties sometimes observed in nano-structured coatings and provides a
general description of the early stages of film growth from nucleation through to the formation of continuous layers. An introduction to the concept of stress in thin films is also included, with possible mechanisms for stress reduction in coatings discussed. The remainder of the chapter gives details on the experimental aspects of this work including discussion of the deposition techniques used to deposit the nano-structured coatings, with details on the system design, and the main characterisation techniques employed in this work.

Chapter 3 investigates the microstructure of Al/AlN nano-structured coatings prepared using a cathodic arc deposition system. The effects on the microstructure of ion bombardment during film growth using a technique known as plasma immersion ion implantation (PIII) is also discussed in this chapter.

Chapter 4 describes two types of multilayers carbon which consists of high and low density a-C, prepared by a cathodic arc deposition system using both DC bias and periodic bias (continuously varying DC bias in a sinusoidal pattern). Two types of multilayers with different interfaces (sharp and graded) are formed and discussed in this chapter.

Chapter 5 presents Al/C multlayers prepared using an unbalanced magnetron sputtering system. The microstructure of the Al/C multilayer films are examined and discussed in this chapter.

Chapter 6 draws an overall conclusion for this work, with a recommendation for future work in this area. Future fundamental research questions are suggested.
1.4 Bibliography


Chapter 2

Background

The mechanical properties of nano-structured materials have received considerable attention in recent years. It is known that as the size of the features (phases in a nanocomposite and layers in a multilayer coating) decreases, there is an increase in the density of interfaces which may result in behaviour different from that of bulk materials. This chapter will review the research progress in nano-structured multilayered films including the explanations for the enhanced hardness observed. A summary of previous studies on multilayer coatings relevant to this thesis is then provided. The types of growth modes observed in thin films and the origin of stress generated during growth is discussed. Finally the methods of synthesizing the thin film including filtered cathodic arc deposition and magnetron sputtering deposition and several analytical techniques such as transmission electron microscopy (TEM), Scanning transmission electron microscopy (STEM), Electron Energy Loss Spectroscopy (EELS), and Auger electron microscopy (AES) will be presented which are used to characterise coatings. The methods for determining the microhardness and stress of the films are also introduced.
2.1 Mechanisms for Enhanced Hardness in Multilayers

There has been a great deal of interest in multilayer coatings due to the unusual combination of mechanical properties and physical properties they can exhibit. These properties are discussed in reviews by several authors [1-4]. It has been reported [5-9] that multilayer coatings can show enhanced hardness and strength above that predicted by a rule-of-mixtures model. In addition, many multilayers appear to show hardness dependence on period, $\lambda$. Several explanations have been proposed to interpret the hardening mechanism including dislocation blocking by layer interfaces [10-11], Hall-Petch strengthening [12-13], coherence strain effects at layer interfaces [14-15] and the supermodulus effect [16-17]. However, the phenomenon of enhanced properties in multilayer coatings is still not clearly understood.

*Strengthening by dislocation blocking*

The first theoretical explanation of the mechanical properties of multilayered materials was provided by Koehler [10]. He proposed that a multilayered structure composed of two metals (A and B) with different dislocation-line energies should resist plastic deformation and brittle fracture well in excess of that for homogeneous alloys. The termination of dislocation motion is energetically favoured for pileup at the layer interface and in the layer with lower shear modulus. He also noted that the layer thicknesses must be thin enough so that dislocation generation can not occur within the layers. Since then, Chu and Barnett [11] proposed a model based on restricted dislocation movement within and between layers in a multilayer coating. It predicts a peak in hardness when there is a difference in shear modulus between two layer materials and sharp interfaces between layers. The model also incorporated the fact that the interfaces in a superlattice are not normally perfectly abrupt and agreed well with the experimental data for hardness [11]. Chu and Barnett’s model provides a basis for choosing materials to achieve an increase in hardness and strength in multilayer coatings.
Hall-Petch strengthening

The Hall-Petch relationship, originally used to explain the increase in hardness with decreasing grain size in polycrystalline metals, can also be applied to explain the hardness enhancements in multilayer by substituting the grain size by the multilayer period ($\lambda$). The modified Hall-Petch relation in multilayer coatings now becomes:

\[ H = H_0 + \kappa \lambda^n \]

where $k$ and $n$ are fitting parameters. The value of exponent $n$ is in the range of 0.2~0.7 depending on the multilayered system. For example, Chu and Barnett [11] assumes that the constituent material has similar crystal structure, and gave a larger exponent of $n \approx 0.7$. Anderson and Li [12] consider only one or two dislocation pile ups near the interfaces and used an exponent of $n \approx 0.3$.

Coherent strain effects

The coherent strain effects [14-15] predicted that alternating coherent stress fields, which exist in multilayer films because of lattice mismatch, can inhibit dislocation motion, leading to the enhancement of strength and hardness of the films. Cahn [14] suggested that dislocation motion, which would allow the material to yield to imposed stresses, is suppressed at interfaces where there is a lattice mismatch. Another variation of this idea is that dislocations are prevented from crossing interfaces between crystals with different slip systems, such as between cubic and hexagonal phases. The barrier to dislocation motions between the two materials may contribute to the hardness of the multilayer.

Coherent strain effects appear to be relatively small compared to dislocation line energy effects [8, 18]. Shinn et al. [18] looked at the effect of differences in the modulus of the two nitride materials and concluded that a difference in elastic modulus between the two layer materials is required to increase the
hardness of the multilayer film, and the coherency strain at the interface between the two layers has only a minor effect.

**Supermodulus effect**

The supermodulus effect remains controversial because researchers have not reached a consensus regarding the effect’s origin, its magnitude or even its sign [19]. Early measurements on metallic multilayers showed large enhancements (~100%) of the elastic constants, a so-called supermodulus effect. Since the hardness is dependent on the elastic properties of a material, this has been used to explain the hardness enhancements. However, attempts to reproduce the results of these studies have shown only small variations in the elastic modulus (~10%) [20-21]. Although there are elastic variations in superlattice, the variations are too small to explain observed hardness and strength enhancement. Therefore it is generally believed that the original reports were due to the difficulty in accurately measuring the elastic properties of thin films.

**Microstructure of layers**

Veprek proposed [22] that crystal/amorphous interfaces should be especially good at suppressing dislocation motion. Dislocations which might form in the crystalline can not move through the amorphous matrix. Crystals a few nanometers size are free of dislocations. The amorphous matrix has to have a high energy of crack formation and propagation at the temperatures at which the materials will be exposed to the load. A randomly oriented nano-crystals embedded within a thin amorphous matrix provides better coherence at the grain boundaries than purely polycrystalline composites. For example, thin films consisting of TiN nanocrystals in an amorphous SiN matrix prepared by plasma chemical vapor deposition have shown a high Vickers hardness of 5000Kg/mm² and elastic modulus of > 500Gpa [22].
2.2 Examples of Multilayer Coatings

Many multilayered systems with different periodicities have been studied in an attempt to produce coatings with superior mechanical properties. Of relevance to this thesis are multilayers with the following combination of materials: metallic/metallic, nitride/nitride, metallic/nitride (carbide), and amorphous carbon multilayered systems.

2.2.1 Metallic/Metallic Multilayers

Metallic/metallic multilayered system are particularly suitable for investigating mechanical properties of nanocrystalline materials, such as residual stress, enhanced hardness and elastic anomalies, especially with regard to grain size and interface effects, since these parameters can conveniently be controlled. The misfit dislocation density, structure, and stress in this system are all rapidly varying functions of the bilayer period. For instance, Lehoczky [9] confirmed Koehler’s theoretical predictions experimentally in Al/Cu multilayer. The results showed the yield stress of the laminates is 4.2 times larger and the tensile fracture stress is about 3 times larger than the values given by the rule of mixtures for Al and Cu. A Hall-Petch like behaviour was also observed in metallic multilayers. For example, this $1/\lambda^{1/2}$ dependence of the hardness of samples of Cu/metal multi-layered systems deposited by a sputtering method was evident obtained by Mirsa et al.[23], which showed that hardness increased with the decrease of layer thickness and became saturated at a thickness of less than about 50nm in Cu-metal systems.

2.2.2 Nitride/Nitride Multilayers

This type of multilayer is considered a good candidate to have enhanced properties due to the nitride, which has complex bonding structure (a mixture of covalent, metallic and ionic components). This gives rise to an interesting combination of physical and mechanical properties, including good wear resistance, chemical inertness and good electrical conductivity. This type of
multilayer is commonly classified into two categories: isostructure and non-isostructure. In isostructural multilayers, generally the individual layers have the same dislocation slip systems due to the same structure and therefore it is possible for dislocations to move across layer interfaces. Various transition-metal nitrides such as TiN, VN, NbN, ZrN, etc, with a cubic structure and a high hardness have been deposited in multilayers with the resulting coatings exhibiting an extremely high hardness. For example, the hardness of epitaxially grown TiN/VN multilayers have been reported to reach a maximum of 5560 kg/mm² at $\lambda = 5.2$ nm [5].

In non-isostructural multilayers, the individual layers have different structures, and different dislocation slip systems, thus providing further barriers to dislocation motion. The analysis of the hardness data is generally more complicated and metastable structures were observed in these multilayers with small layer thickness ($\leq 2$ nm). For TiN/AlN multilayers, the AlN layer which is normally hexagonal was found to exist in the cubic NaCl-type structure for layer thicknesses below ~2 nm. This resulted in a coherent interface with the TiN and the hardness was seen to increase dramatically up to ~40 GPa (4000 kg/m²) [24]. This rocksalt structure B1-AlN was also observed in an AlN/VN superlattice with layer thickness of less than 4.0nm [25].

Figure 2.1(a) shows the evolution of the hardness H as a function of increasing $\lambda$ in selected nitride/nitride multilayers. Generally a maximum value is reached around 2-8nm, after which in some cases the hardness decreases with further decrease in $\lambda$. However, it is clear that there is no general curve as a function of period. One problem is that many studies [26-27] do not examine the microstructure of the coatings to ensure that a multilayer structure is produced as desired. Problems can arise, particularly at the small periods, where depending on the growth mode, individual layers may not form and a mixed or nanocomposite coating results.
Figure 2.1 Hardness evolution as a function of the period $\lambda$ in
(a) Nitride/nitride multilayered systems, (b) Metallic/nitride multilayered systems.
2.2.3 Metallic/ Nitride Multilayer Coatings

This type of multilayer combines a hard nitride with a more ductile metal and has been reported to exhibit improved toughness and high-temperature stability compared to nitride/nitride systems, while retaining a relatively high hardness ($\geq 20$GPa) [30]. In these multilayer systems, dislocation motion across layer interfaces is difficult since the layers typically have different crystal structures and provide interface barrier strengthening. Figure 2.1(b) shows the hardness $H$ as a function of increasing $\lambda$ in some metallic/nitride systems. Again there is a large spread in the results with no common period in which a maximum occurs.

2.2.3.1 Preliminary Observations on Ti/TiN Multilayer

(This work was conducted in collaboration with Mr. Luke Ryves at the University of Sydney. Ti/TiN multilayer sample deposition and hardness measurements were performed by him, TEM sample preparation and TEM observations were carried out by the author)

Figure 2.2 showed the TEM image of a Ti/TiN multilayer prepared using cathodic arc deposition. A multilayer structure is clear, but in some regions it is hard to resolve the individual Ti or TiN layer due to the similar contrast. A columnar microstructure appears across the interfaces of multilayer, especially in the dark field image in figure 2.2(b). The electron diffraction pattern, shown in figure 2.2(c) presents two close diffraction rings which are due to presence of both $\{0002\}$ titanium metal and $\{111\}$ titanium nitride. The dark field image shown in figure 2.2(b) is taken using both $(111)_{\text{TiN}}$ or $(0002)_{\text{Ti}}$ reflection spots. Since the lattice d-spacing between $\{111\}_{\text{TiN}}$ and $\{0002\}_{\text{Ti}}$ are very close ($d_{(111)_{\text{TiN}}}=0.2443$nm, $d_{(0002)_{\text{Ti}}}=0.2343$nm) and are only separated by 0.1Å, this leads to minimal strain between the two structures, enabling the epitaxial growth of one material on the other. Epitaxial growth between the $\{111\}$ oriented TiN layers and the $\{0002\}$ oriented hexagonal Ti layers appears to produce a system of strong columnar grains oriented normal to the substrate. These columnar features are in most cases approximately crystals which reflect coherence with the other layers within the columns.
Figure 2.2 (a) Bright field image of the Ti/TiN multilayer structure for a coating with $\lambda=25\text{nm}$, (b) Dark field image taken using the $(111)_{\text{TiN}}$ or $(0002)_{\text{Ti}}$ diffraction spots, (c) Diffraction pattern of the TiN/Ti multilayer.
Figure 2.3 shows the hardness as a function of multilayer period as measured using nanoindentation. The hardness of all samples was found to be the same as the hardness of the silicon substrate. The lack of hardness enhancement in Ti/TiN multilayer may arise from columnar structure and epitaxial growth. The observed columnar structure and epitaxial growth was reported in a TiN single layer [35] and also affected the indentation test.

This result showed the importance of carefully choosing materials for constituent multilayer films which have dissimilar crystal structures to prevent epitaxial growth between constituent materials in a multilayer system or it is necessary to select two materials where the d-spacing of them at the interface are not so similar to overcome this.

![Figure 2.3 The hardness as a function of period \( \lambda \) in Ti/TiN multilayer films.](image)

### 2.2.4 Amorphous Carbon Based Multilayered Coatings

A material which has received much attention over the last decade is amorphous carbon. Amorphous carbon (a-C) can come in various forms with properties which depend on the ratio of diamond-like \((sp^3\) hybridised) to
graphite-like ($sp^2$ hybridised) bonding present. Typically, a-C films contain mainly $sp^2$ bonding, is relatively soft and has a density of between 1.8 and 2.3 g/cm$^3$. When rich in $sp^3$ bonds, the material is called tetrahedral amorphous carbon (ta-C). Ta-C has a $sp^3$ bonding fraction of approximately 80%, a density of approximately 3 g/cm$^3$ and hardness comparable to diamond. It also has a low friction coefficient, good wear resistance and is chemical inert. As a result of these favourable properties the ta-C films could be useful for electronic, optical and mechanical applications.

A major limitation of a-C films, particularity as the $sp^3$ fraction increases, is that they exhibit high intrinsic compressive stresses which limit the thickness of the film and inhibit practical applications. Therefore, it is difficult to deposit a ta-C film with simultaneous low compressive stress, high hardness and high film thickness. Recently it has been shown that the reduction of the stress in thick a-C films with high hardness and good tribological behaviour can be achieved by developing a multilayered structure (consisting of sequential soft and hard layers) [36]. These multilayer structures can exhibited a lower wear rate than monolithic films and improve the films’ hardness. Examples include multilayers of a-C/ta-C [37–40], metallic/a-C [41–44] and a-C/TiC$_x$ and a-C/WC$_x$ [45]. Further descriptions are presented in section 4.0, chapter 4 and section 5.0, chapter 5.

2.3 Growth Modes for Thin Film Formation

A decisive period of film growth is the nucleation stage at the very beginning of the film deposition. The growth mode of a film is influenced by two parameters: the total surface free energy per unit area and the lattice constants of the substrate and the film. For the determination of the growth mode the surface free energies of the substrate $\gamma_{sub}$, of the interface $\gamma_{int}$ and of the film $\gamma_{film}$ are important. If the sum of the film and interface free energies is larger than the substrate free energy: $\Delta\gamma = \gamma_{film} + \gamma_{int} + \gamma_{sub} > 0$, film grows in 3-dimensional islands instead of a complete layer. If the sum of the film and interface free
energies is smaller than the substrate free energy: \( \Delta \gamma = \gamma_{film} + \gamma_{int} + \gamma_{sub} \leq 0 \), film wets the substrate completely and film growth proceeds via the formation of 2-dimensional islands in a layer by layer fashion. If \( \Delta \gamma \) changes its sign with increasing film thickness, for thin film \( \Delta \gamma \) is smaller than zero, which results in layer growth, but for a thicker film \( \Delta \gamma \) becomes larger than zero, the island growth occurs. Three different growth modes are illustrated in figure 2.4 [46]. Island growth can be useful for growing nanostructures on a surface. Layer-by-layer growth requires higher mobility of adatoms than island growth.

![Figure 2.4 A schematic illustration of the three growth modes for thin film](image)

(a) Island mode (Volmer-Weber mode), (b) Layer-by-layer mode (Frank-van der Merwe mode), (c) Layer then island mode (Stranski-Krastanov mode).

### 2.4 Origin of Stress in Multilayers

Stress in compositionally uniform thin films can be classified as either coherency, extrinsic (or thermal) and intrinsic (or growth). A coherency stress results when a thin film has a lattice matched with the substrate i.e. the substrate has an equilibrium in-plane lattice parameter different from that of the film. Extrinsic or thermal stresses arise from the difference in thermal expansion coefficient between film and substrate materials, and can be evaluated by the following equation [46-47]:

\[
\sigma = \frac{E}{1 - \nu} (\alpha_f - \alpha_s) \Delta T
\]  

(2.2)
where $E$ is the Young's modulus, $\nu$ is the Poisson's ratio, $\alpha_f$ is the thermal expansion coefficient of the film, $\alpha_s$ is the thermal expansion coefficient of the substrate, and $\Delta T$ is the temperature difference between the deposition or heat treatment temperature and the room temperature.

Intrinsic stresses are generated during film growth that is not a result of coherency or thermal effects. The energetics of the PVD process strongly influence the crystallographic texture, resulting microstructure as well as interface structure and roughness, which in turn affect the film properties such as film adhesion, crack behaviour. Also the stresses may have some effect on the growth mode [48] and compressive stresses appear to be an intrinsic part of growth process [49]. Understanding the origin of stress and the ability to control the level of stress is of great importance for industrial applications.

Various investigations [50-62] have been performed to explain the intrinsic stresses. The first systematic investigations by Thornton and Hoffman (TH) [48, 50] showed that a stress can change from tensile to compressive stress when varying the deposition condition and identified the energy of the depositing particle and flux as the fundamental quantities which determine the nature and the magnitude of the stress. Davis [54] presented a simple mathematical model to explain the formation of compressive stress in thin film deposited with simultaneous bombardment by energetic ions or atoms. The model predicted that the magnitude of the compressive stress is strongly dependent on the ion energy, with the form of the energy dependence determined by the normalized flux $j/R$, where $R$ is the net depositing flux and $j$ is the bombarding flux. Further description about Davis’ model will be presented in section 4.2.3.1, chapter 4.

Ruud et al. [61] discussed that the stresses in multilayers could result from several reasons: growth process, differences in thermal expansion between film and substrate, coherency strains, interfacial reactions, and the interface stress. They investigated bulk and interface stresses in Ag/Ni multilayers. A relation was developed by minimizing the energy due to the uniform straining of the
multilayers. Their relation shows that the total measured stress of a multilayered film mainly results from two terms, the bulk deposition stress in the layers and the interface stress. Awano et al. [62] also argued that the interface stress (caused by surface free energy) is important for the total residual stress of a multilayered film. Thus, the introduction of interfaces by a multilayered structure may reduce the high residual stress in multilayer coatings.

Cammarata [63] also described the stress in multilayered films. He thought stress generation of the types described above for compositionally uniform overlayers can also occur in multilayered thin films. In the case of thermal stress, the stress equation given above (see equation (2-2)) holds for each layer, independent of the other layers, so long as the total film thickness is much less than the thickness of the substrate. Coherency stresses in multilayers in which there is lattice matching at the interfaces between the layers can lead to interesting thermodynamic behaviour, such as violation of the Gibbs phase rule and the common tangent rule for determining multilphase equilibrium from free energy versus composition diagrams [64].

The average stress in a multilayered thin film may be rather similar to that in a uniform thin film, their stress are a combination of stress values of each individual layer within the film. What is very special about a multilayer is that there can be alternating tensile and compressive stresses in the individual layers. Even when the average stress is small these layer stresses can be quite large. This will result in large stress gradients in the film and these act as an additional driving force for atomic diffusion. Such a thermodynamic effect is quite distinct from the kinetic effect represented by the activation volume.

### 2.5 Fabrication Methods

Generally, there are two main types of techniques commonly used for fabricating thin films: chemical vapor deposition (CVD) and physical vapor deposition (PVD). CVD involves chemical reactions which transform gaseous
molecules into a solid material in the form of a thin film or a powder on the surface of a substrate. Physical vapor deposition (PVD) contains the physical change of state of the material that is being deposited (target material). The thin film is made in vacuum by condensation from a flux of neutral or ionized atoms. Examples of PVD techniques are filtered cathodic vacuum arc, ion-beam assisted deposition, magnetron sputtering, thermal evaporation deposition, and pulsed laser deposition. In this work, PVD techniques including magnetron sputtering and filtered cathodic arc deposition are used to prepare the coatings, these are described below.

2.5.1 Magnetron Sputtering

Magnetron sputtering is a plasma vacuum coating technique, particularly suitable for industrial applications [65]. Figure 2.5 presents a schematic diagram of the conventional magnetron sputtering. Magnets are placed behind the target. The energized plasma ions strike a "target", which acts as a cathode and is composed of the desired coating material. The ions cause atoms from that target to be ejected with enough energy to travel to, and bond with, the substrate. Secondary electrons are also emitted from the target and they play an important role in maintaining the plasma. In conventional magnetron sputtering, the plasma is strongly confined to the target, with a region of dense plasma extending some 60 mm from the target surface. Substrates positioned within this plasma will be subjected to concurrent ion bombardment; this strongly influences the structure and properties of the growing film. Substrates placed outside this plasma, however, will lie in an area of lower plasma density, and experience insufficient ion bombardment to modify the microstructure of the growing film. Therefore it is, difficult to produce fully dense, high quality coatings on large, complex components using conventional magnetrons [65]. Therefore this technique has some disadvantages including the low deposition rates, relatively low ionization efficiencies in the plasma and high substrate heating effects. These problems have been overcome by development of the unbalanced magnetron, and its incorporation into multiple-magnetron systems. The closed-field unbalanced magnetron sputtering technique has now been
used to deposit high quality coatings of a very wide range of materials. Metals, alloys, ceramics, multilayers and functionally-graded materials can all be deposited with excellent properties [66]. Furthermore the pulsed magnetron sputtering [67] has also been developed for the deposition of highly insulating materials in order to overcome arc discharges during the deposition process.

2.5.2 Cathodic Arc Deposition

The cathodic arc is a low-voltage, high current plasma discharge that takes place between two metallic electrodes in vacuum. The cathodic arc deposition system includes a cathode made of a film forming material, a striker that produces the arc, an anode, a vacuum chamber having the cathode and the anode therein, and a substrate holder. A film is formed on the substrate by generating an arc discharge between the cathode and the anode (shown in figure 2.6).

The arc discharge also produces small liquid droplets commonly referred to as macroparticles which are ultimately incorporated into the coating. These macroparticles prevent the application of the arc evaporation process to the more demanding areas of precision optics and electronics. For this reason considerable efforts have been made in recent years to reduce or eliminate droplets using various forms of macroparticle filters [68-70]. The most successful of those are based on the use of a curved plasma duct filter. These employ electro-magnetic and mechanical filtering techniques to remove
unwanted macro-particles and neutral atoms. Only ions within a defined energy range reach the substrate, thus producing films with good controllability and reproducibility. This technique is known by the name of filtered cathodic arc deposition.

Figure 2.7 shows the diagrams of the filtered cathodic arc deposition system situated at both the Sydney University (figure 2.7(a)) and RMIT University (figure 2.7(b)) used in this work. These deposition systems compose of cathode source, an anode, a substrate holder, magnetic filters, vacuum system and substrate bias power supply. The difference between the two deposition systems is that Sydney system used a 90° curved solenoid duct, while the RMIT system had a double bend solenoid duct and a computer controlled substrate bias system.

The substrate bias is important part in the cathodic arc deposition system since it can be used to modify the coatings. A DC negative bias voltage, a pulsed negative bias voltage and periodic bias voltage were used in this work. When pulsed negative-bias voltages are applied to the substrate, the technique is called plasma immersion ion implantation and deposition (PIIID). PIII is a hybrid process combining cathodic arc deposition and plasma immersion ion
Figure 2.7 Schematic diagrams of cathodic arc deposition used in this work (a) located at Sydney university (top-view), (b) situated at RMIT University (side-view) [71].
Figure 2.8 Schematic diagram of plasma immersion ion implantation and deposition (a) No ion implantation when bias equals 0, leading to a sharp interface; (b) Ion implantation takes place during pulses, modifying the interfaces.

implantation [72-74]. Figure 2.8 illustrates the basic idea of PIII: when the bias equals zero kV, no ion implantation takes place (see figure 2.8(a)), films are deposited with ions in the energy range of 20-50 eV and a sharp interface is produced. When negative bias is applied to a conductive substrate, an electric field (sheath) is formed around the substrate and the ions that are accelerated through the sheath are implanted into the substrate with additional energy provided by the bias applied, resulting in a diffuse interface shown in figure 2.8(a). Ion bombardment strongly influences film growth and the physical, chemical, structural and mechanical properties of the final coating. The high deposition energy of the condensing species is essential in film growth: promoting adhesion and also disrupting columnar growth [75].

2.6 Analysis Methods

To understand how the microstructure of the deposited materials relates to the mechanical behaviour of the thin film, which in turn determines the practical use of a coating, it is important to characterise the film and measurement of mechanical properties. In this section, a brief of description of transmission electron microscopy (TEM), X-Ray diffraction, Auger electron spectroscopy (AES) and Raman spectroscopy and how they are used to characterise the microstructure and composition of multilayers at atomic level will be given.
Further techniques of Nano-indentation and stress measurements will be described.

### 2.6.1 TEM Analysis

Conventional TEM can provide the direct observation of the nano-structured coatings and gives a detailed description of the microstructure including grain size, orientation and texture. High resolution TEM can offer atomic scale information on the structure of the layers and interface characteristics such as coherency and morphology. Scanning transmission electron microscopy (STEM) techniques can provide imaging and spectroscopic information, either simultaneously or in a serial manner, of the specimen with a spatial resolution of the order of one nanometer.

In this project, microstructure observation was carried out in a JEOL 2010 Transmission Electron Microscope fitted with a Gatan Imaging Filter (GIF), which was attached under the camera chamber. The microscope is an analytical STEM equipped with LaB6 cathode and operated at 200KeV. Bright film images, dark film images and diffraction patterns were used to investigate the microstructure of the coatings. Electron Energy Loss Spectrum (EELS) and STEM EELS spectrum image were also used to study the coatings.

#### 2.6.1.1 Cross-sectional TEM Sample Preparation

The TEM sample is required to be thin enough to let the electron beam transmit through the sample and form the image. In my thesis, all the TEM samples were prepared with a wedge-shape using a tripod polisher. The wedge mechanical polishing technique results in the thinnest part of sample being at the edge. This technique showed no artefacts introduced from the sample preparation procedure according to the John M. Phelps’s report [76]. Some area of the sample may be lost due to over polishing. Figure 2.9 shows the process of preparing a cross-sectional TEM sample of a thin film sample. Two sample slices and two silicon slices are glued together with the films face-to-face using an epoxy resin as shown in figure 2.9(b). The resulting “sandwich” is mounted
onto a tripod polisher with wax, ground and polished both sides using diamond discs with different-sized of 30μm, 9μm, 3μm and 1μm. The first side is polished until a flat, mirror-like surface with little damage is obtained. The second side of the specimen is prepared at a slight angle, known as the “wedge angle β”, shown in figure 2.9(c). The magnitude of this angle dictates the amount of thin area which will be available from the front edge to the back edge of the specimen. The wedge angle β of approximately 0.5° was used. After polishing the wedge-shape sample is shown in figure 2.9(c). The front edge or the thinnest part is about 10μm or less than 10μm thick. A wedge-shape sample is

Figure 2.9 Schematic diagrams illustrating the process of preparing cross-sectional TEM samples.
then cut and glued to a copper support ring as shown in figure 2.9 (d). In the final step, the thinnest part of sample is ion-beam-thinned using a GATAN Precision Ion Polishing System (PIPS) model 691 for about 15 minutes. The thickness of the thinnest parts of each specimen was estimated to be approximately 50nm after ion-beam thinning. The cross-sectional TEM sample of the thin film is now ready for TEM observation.

2.6.1.2 Electron Energy Loss Spectroscopy

When a beam of energetic electrons passes through a layer of material, it loses part of its energy due to inelastic scattering on atomic electrons of material. Electron Energy Loss Spectrum (EELS) involves the measurement of the energy lost by the electron beam in a specimen. A typical EELS spectrum from BN is plotted in figure 2.10, illustrating the three main parts including the zero loss, low loss valence band excitations and the inner shell edges (core loss). The first zero loss or “elastic” peak represents electrons which are transmitted without suffering any measurable energy loss. The low loss region from 5-50eV is dominated by Plasmon peaks, which result from a collective excitation phenomenon of electrons in the conduction band of the atoms in the sample. Compared to the Plasmon generation, the inner-shell ionization is a much less probable process, leading to a low intensity of the peaks. At higher energy loss, the amount of inelastically scattered electrons drastically decreases with increasing energy loss, thus small peaks are superimposed on a strongly decreasing background (spectrum). Because of the low intensity, the representation of the high-loss region is often strongly enhanced (see figure 2.10). For the ionization of atoms, a specific minimum energy, the critical ionization energy Ec or ionization threshold must be transferred from the incident electron to the expelled inner-shell electron, which leads to ionization edges in the spectrum at energy losses that are characteristic for an element. Thus, EELS can be utilized for qualitative and quantitative element analysis as well. In particular, the detection of light elements is a main task of EELS.
EELS was used to carry out energy-selected imaging (ESI) and energy filtered TEM (EFTEM) by selecting only the inelastically scattered electrons corresponding to the inner shell losses of the element edge of interest [77]. A three window background subtraction technique was used to remove the background contribution. Two windows are placed in front of the edge and one below the edge. Pre-edge windows are used to evaluate the background parameters so that the background contribution to the post-edge can be calculated. The spectra and the images were acquired by a CCD camera integrated in GIF and all data processing was performed using the Gatan Digital Micrograph software.

![Energy loss spectrum from BN](image)

Figure 2.10 An example of an energy loss spectrum from BN, illustrating the zero loss, the peak of low loss region and the inner shell or core loss edges. A scale change of 1000× was introduced at 100eV for display purpose.

2.6.1.3 Estimation of Atomic Density in Carbon Materials Using Low Loss EELS

By measuring the energy $E_\rho$ of the Plasmon peak in the low loss region, the density of specimen can be estimated using a free electron model, which is described by the following equation [77]:

$$E_\rho = \hbar \omega_\rho$$  \hspace{1cm} (2-3)
\[ \sigma^\ast = \frac{N_e e^2 \rho}{\varepsilon_0 m^*} \quad (2-4) \]

where \( h \) is Plank’s constant divided by \( 2\pi \), \( m^* \) is the effective mass, which differs from the rest mass \( m \) of the electron; \( \omega_\rho \) is the plasma frequency; \( N_e \) is the electron density, i.e. the number of free electron per cm\(^3\) which contributes to the valance band Plasmon; \( \varepsilon_0 \) is the permittivity of free space. In the case of carbon sample, it can be assumed that each carbon atom furnishes four valance electrons to the solid, using \( m^* = 0.87m \), as was proposed by Ferrari et al. [78], it is possible to relate \( E_\rho \) to the mass density \( \rho \) (in g/cm\(^3\)) using:

\[ \rho = 3.139 \times E_\rho^2 \times 10^{-3} \quad (2-5) \]

2.6.1.4 Measurement of the Fraction \( sp^2 \) Bonding Using Carbon K edge

A typical carbon K-edge EELS spectrum is shown in figure 2.11 after removal of the background. The edge consists of a peak at 285eV due to the excitation from \( 1s \) to empty \( \pi^* \) states of \( sp^2 \) sites, followed by a step at around 289eV due to transitions from \( 1s \) to empty \( \sigma^* \) states of both \( sp^2 \) and \( sp^3 \) sites. The calculation of the fraction of \( sp^2 \) bonded carbon atoms in carbon-like materials is made by comparing the contribution of the \( 1s \) to empty \( \pi^* \) peak in the carbon K-edge spectra to that of a standard which can be considered 100% \( sp^2 \) bonded. Integration of the counts in the \( \pi^* \) peak at 285eV fitted by a Gaussian gives values which are proportional to the number of \( \pi^* \) bonded electron in the materials. The fraction of \( sp^2 \) bonded is calculated by [79]:

\[ f = \frac{I_{g\pi^*} I_u(\Delta E)}{I_{u\pi^*} I_g(\Delta E)} \exp(t/\lambda_\rho) \quad (2-6) \]

where \( I_{g\pi^*} \) and \( I_{u\pi^*} \) are the integrals from the leading edge to the \( 1s \) to \( \pi^* \) peak of the standard and unknown carbons respectively. \( I_g(\Delta E) \) and \( I_u(\Delta E) \) are the integrals over some energy window \( \Delta E \) (normally \( \Delta E = 284\text{-}310\text{eV} \)), of the standard and unknown carbons. The factor \( \exp(t/\lambda_\rho) \), known relative thickness, is applied to correct for multiple scattering which tend to reduce the intensity.
Figure 2.11 A diagram of typical carbon K-edge EELS spectrum after removal of the background, consisting of a $1s \rightarrow \pi^*$ peak at 285eV and a $1s \rightarrow \sigma^*$ inflection point.

of $\pi^*$ peak and is determined from the low-loss spectra in the normal way [77]. Here $t$ is the specimen thickness and $\lambda_p$ the Plasmon mean free path.

2.6.1.5 STEM EELS Spectrum Imaging

EELS contains information on the local bonding state and atomic environments at each location in the sample. Software control of the electron beam and EELS allows the production of elemental maps or profiles through thin film coatings and interface regions. Many modern TEMs are able to operate in a scanning mode. Scanning TEM or STEM involves the scanning of a very fine electron probe over an area of a specimen. Images can be generated using the unscattered intensity or scattered intensity through the annular detector as the electron beam is rastered over the area of interest. As shown schematically in figure 2.12, it is also possible for an Electron Energy Loss Spectrometer to measure an EELS spectrum from the region of sample being probed by the electron beam. Figure 2.13 illustrates a series of low loss EELS spectra collected across an interface.
Figure 2.12 Schematic diagram of the detector arrangement in STEM spectrum imaging mode.

Figure 2.13 Examples of a series of low loss EELS spectra collected by scanning the beam across an interface.
The spatial resolution of STEM imaging is determined by the size of electron probe used to illuminate the specimen. Modern STEM Instruments are capable of producing electron probes at sub-nanometer spatial resolution so that atomic resolution images can be obtained. In this project, all EELS line-scan data are taken with a probe size of approximately 5nm.

2.6.2 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a widely used analytical technique for obtaining the chemical composition of samples which is especially sensitive to the composition of thin surface layers. Samples are bombarded with electrons accelerated in electron gun to energise in the range 1 to 10kV. Auger electrons are emitted from the sample as a result of relaxation of atoms ionised by the incident electron beam. The energy of the Auger electron is characteristic of the particular element it originated from. Therefore AES can be used to determining the composition of a sample. In addition to surface stoichiometry, an elemental depth profile can be obtained by using an ion beam to sputter away atoms from the surface of a sample. An inert gas (usually Argon) is used as the sputtering ions and the measurements are performed in an ultrahigh-vacuum chamber to prevent surface contamination.

The typical information depth for Auger is in the range of 30-60Å, with a spatial resolution in 10nm range at best, but normally the resolution is in the order of 100 nm. In the case of sputter depth profiles, the sputter time may affect the depth resolution. The more material that is removed, the rougher the surface becomes and the depth resolution deteriorates, particularly after long sputter times.

For the work described in this thesis Auger depth profiling was performed on a Scanning Auger Nanoprobe VG310F with 3 keV ion beam.
2.6.3 Raman Spectroscopy

Raman spectroscopy is a standard non-destructive tool for structural characterization, particularly suitable for the study of carbon materials [80-81]. As mentioned in section 2.2.4, the great versatility of carbon materials arises from the ratio of $sp^2$ (graphite-like) to $sp^3$ (diamond-like) bonds present. There are many forms of $sp^2$-bonded carbons with various degrees of graphitic ordering, ranging from microcrystalline graphite to glassy carbon. In general, the Raman spectra of all carbons show several common features in the 800-2000 cm$^{-1}$ region. The so-called G and D bands, which lie at around 1560 and 1360 cm$^{-1}$ for visible excitation are due to $sp^2$ sites only. The G-band is due to the bond stretching of all pairs of $sp^2$ atoms in both rings and chains [82]. The D-band is due to the breathing modes of $sp^2$ atoms in rings. The positions, widths, and relative intensities of these two features are found to vary systematically with deposition conditions and film properties. Figure 2.14 shows the typical Raman spectra of ta-C [83] and glassy carbon [84]. In ta-C film, a broad peak of G-band is observed at approximately 1550 cm$^{-1}$. In contrast, in glassy carbon, both the G-band and D-band are clear visible, indicating a microstructure which contains more ordered graphite structure.

The spatial resolution of a Raman instrument is mainly determined by the optics and the wavelength of the laser. The smaller the wavelength and the larger the numerical apertures of the objectives of the microscope, the smaller the focused beam spot. In theory, spot sizes as small as 0.4 $\mu$m can be obtained. However, in practice the spot size is always larger than the theoretically predicted one, due to bad alignment or focusing.

Raman spectra were collected in this project using a Micro-Raman Instrument (T64000, Atago-Joban Yvon) with 514.5 nm Ar$^+$ excitation and a laser beam diameter of 2 $\mu$m diameters. The laser power was 20 mW/cm$^2$. 

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2.6.3 X-Ray Diffraction (XRD)

X-ray diffraction is widely used as a multilayer structural characterization tool for determining bilayer period, intermixing, stress, and texture in multilayer structures. X-ray analysis and the different TEM techniques provide complementary information to form a complete structural description of the multilayers to aid in the understanding of their mechanical properties.
In this work, XRD was performed on Bruker D8 XRD using Cu Kα (1.54056Å) radiation (35Kv, 40mA), scan width 2θ is from 30° to 50°, step size is 0.02°, and counting time were used 1s per size.

### 2.6.5 Film Thickness Measurement

In order to measure the film thickness, several dots were marked on the Si wafer before deposition. These markers were then erased using alcohol after deposition. A Tencor-16 surface profiler was used to scan across the boundary of the uncoated and coated area of the marked portion of the silicon wafer, providing the film thickness.

### 2.6.6 Mechanical Property Measurements

Good mechanical properties of a coating require high hardness, high toughness, low friction, high adhesion strength on substrate, good load support capability and chemical and thermal stability. Of all these, Elastic modulus and hardness are probably the most important for industrial coatings. The elastic modulus often determines the level of residual stress in the film arising from the deposition process and the subsequent strength of adhesion of the film to the substrate. The hardness determines the resistance of the film to plastic deformation.

#### 2.6.6.1 Measurement of Hardness and Elastic Modulus

Indentation is regarded as a good method in hardness determination of thin films and coatings. Today, the most widely used method for indentation is that of Oliver and Pharr [85], which expands on ideas developed by Loubet et al. [86], and Doerner and Nix [87]. In this method, a small indentation was made with a Berkovich indenter as the indentation load, \( P \), and displacement, \( h \), are continuously recorded during one complete cycle of loading and unloading. Figure 2.15 is a typical indentation load-displacement curvature. The key quantities are the peak Load, \( P_{\text{max}} \), the displacement at peak load, \( h_{\text{max}} \), and the initial unloading contact stiffness, \( S=dP/dh \), i.e. the slope of the initial portion of
the unloading curve. From the loading and unloading curves nanomechanical properties including the nanohardness and elastic modulus can be extracted. The detailed procedures of nanoindentation with this type of instrument have been described by Oliver and Pharr [85]. The indentation hardness is determined from the load data using the relation:

$$H = \frac{P(h)}{A(h)}$$ (2-7)

Where $P(h)$ is the measure load, $A(h)$ is the projected area of the indent as function of the plastic depth $h_p$ and is estimated by evaluating an empirically determined indenter shape function at the contact depth. For a three-sided pyramidal Berkovich indenter with an included half-angle of 65.3°, the relationship [87] between the projected area $A$ of the indentation and the depth $h_p$ beneath the contact is:

$$A = 3h_p^2 \tan^2 65.3 = 24.5h_p^2$$ (2-8)

Once $h_p$ is known, then the projected area of contact is thus calculated and the hardness at load $P$ is computed from the mean contact pressure. The plastic depth $h_p$ is deducted as following [88]:

$$h_p = h_{max} - \left[ \frac{2(\pi - 2)}{\pi} \right] \frac{P_{max}}{dP/dh}$$ (2-9)

where $P_{max}$ and $dP/dh$ are experimentally measured quantities.

$$P = \frac{1}{2} \frac{dP}{dh}$$ (2-10)

$$E = \frac{dP}{dh} \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}}$$ (2-11)

For an elastic contact, the relationship between the load $P$ and the depth of penetration for a cone of semi-angle $\gamma$ is given by:

$$P = \frac{\pi}{2} E' \alpha^2 \cot \gamma$$ (2-12)
where the $\alpha$ is the radius of the circle of contact, the quantity $\alpha \cot \gamma$ is the depth of penetration $h_p$ measured at the circle of contact and $E^*$ is the combined modulus of the indenter and specimen given by:

$$\frac{1}{E^*} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i}$$

(2-13)

where $v$ and $E$ are Poisson's ratio and elastic modulus of the specimen, respectively; and $v_i$ and $E_i$ are Poisson's ratio and elastic modulus of the diamond indenter, respectively.

In this work, the hardness of nano-structured films was measured using a Hysitron Tribo-Indenter with a standard Berkovich diamond indenter, three-sided pyramid diamond indenter with nominal angle of 65.3° between the tip axis and the faces of the triangular pyramid, which was forced into the specimen surface by using a coil and magnet assembly. The load was applied to the surface while constantly monitoring the displacement $h$ of the tip. In order to avoid substrate effects and reduce the error, specimens were typically
relatively smooth and flat. The load used in the hardness measurement was chosen to be sufficiently small (200μN-1200μN) so that the penetration depth was less than one-fifth of the film thickness [85].

2.6.6.2 Stress Measurement

The stress can be tensile or compressive depending on the deposition condition and may lead to effects such as film cracking or film delamination. Figure 2.16 illustrates the tensile and compressive stress in a thin film which arises from the bending of the substrate. This stress is bi-axial in the plane of the film, with little stress in the third direction to the free surface. The bending direction represents the sign of stress. By measuring the amount of bending, δ using a Tencor-16 surface profiler, the stress in the specimen can be calculated by Stoney’s equation [89]:

\[
\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f} \left[ \frac{1}{R_f} - \frac{1}{R_s} \right]
\]

(2-14)

\[
\sigma = \frac{8E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f} \frac{\delta}{L^2} \text{ if } L >> \delta
\]

(2-15)

- \(E_s\) is Young’s modulus of the substrate (about 125GPa for Si)
- \(\nu_s\) is Poisons ratio of the substrate (about 0.28 for Si)
- \(t_s\) represents the thickness of the substrate
- \(t_f\) represents the thickness of the coating
- \(R_f\) represents the radius of the curvature of the coated
- \(R_s\) represents the radius of the curvature of the uncoated substrate
- \(L\) represents the scanning length of substrate
- \(\delta\) represents the bending of the substrate after coating
Figure 2.16 Schematic illustration of a wafer bowing due to residual stress in a thin film for (a) tensile stress, (b) compressive stress [90].

2.7 Bibliography


65. S. M. Rossnagel, Sputter Deposition. In: W.D. Sproul and K.O. Legg Editors,


83. Our research group data (unpublished).


Chapter 3

Synthesis and Characterization of Al/AlN Nano-structured Coatings

This chapter explores Al/AlN nano-structured coatings fabricated using a filtered cathodic arc deposition system. Cross-section TEM(X-TEM) is employed to examine the coating microstructure. Auger depth profiling is used to determine stoichiometry and the levels of any impurities in the coatings. Nanohardness and stress of the Al/AlN nano-structured coatings is also measured to assess the properties of multilayers.

This chapter also explores the effects on the microstructure of applying high voltage pulses to the substrate during deposition, using a technique known as plasma immersion ion implantation. A model is developed to explain the aggregation process which leads to nanocomposites rather than multilayers. This process is limited by diffusion depending on the growth rate and the presence of ion bombardment.

Some of the work in this chapter has been published in the following paper:

3.0 Introduction

Aluminum nitride has some outstanding physical properties, such as high thermal conductivity, low thermal expansion coefficient, high hardness and electrical resistivity, as well as a high surface acoustic wave velocity and a piezoelectric character. Owing to these unique properties, Aluminum nitride (AlN) thin films have attracted much interest and are considered to be one of the most useful materials applied to electrics fields. However, Al/AlN nano-structured coatings have been investigated only by several authors [1-4]. In some cases, the indentation properties were intermediate between the two materials [1-3] and in others they exceeded the properties of both [4]. At present, there are no reported investigations of the nature of the microstructure in Al/AlN coatings.

In this chapter, Al/AlN nano-structured coatings are synthesised using cathodic arc deposition. Al/AlN system is interesting since there is a large mismatch in modulus between them, the modulus of Al is 70.5GPa and the modulus of AlN is 317-344GPa [5]. Emphasis is placed on understanding the effect on the microstructure of varying the deposition conditions. This is accomplished by observing the microstructure, measuring the average stress and testing the composition and hardness of the coatings. Furthermore, we investigate the effects on the microstructure of applying high voltage pulses to the substrate during deposition, using a technique known as plasma immersion ion implantation (PIII).

3.1 Experimental Details

Al/AlN multilayers were deposited using the cathodic arc deposition system at Sydney University described in chapter 2.5.2. The cathode was a 50-mm diameter aluminum disc of purity 99%. The substrates were (100) Si of thickness 300-400 micrometers and were ultrasonic cleaned using ethanol and acetone before inserting into the chamber. Prior to deposition, the deposition system was evacuated to a vacuum base pressure of 2x10⁻⁵Torr. For synthesis
of the Al/AlN multilayers, N₂ gas was injected in the space of the cathode and the flow was alternately turned on and off. The thickness of the Al and AlN bilayers was controlled by varying the deposition time of each layer for a given deposition rate. In order to stabilize the plasma, Ar background gas was admitted at flow rates of 2.0sccm and 5.0sccm for Al and AlN layers, respectively. In all cases, the first layer to be deposited was Al. A one minute pause was inserted between the deposition of alternate layers of Al and AlN to allow the gas pressure to stabilize. Sample sets with different bilayer thicknesses, \( \lambda \), and two deposition rates for Al and AlN were fabricated as shown in table 3.1. Series L samples were deposited at a low deposition rate, while series H samples were deposited at high deposition rate. The AlN layers in series C samples were deposited while applying 8 kV bias pulses of length 20 \( \mu s \) at a frequency of 800 Hz to the substrate holder as described in section 2.5.2. The application of pulse bias to the substrate is known as plasma immersion ion implantation (PIII). The total thickness of each multilayer in all three series was kept between 150 and 200nm. The deposition conditions are summarized in table 3.2. The arc current was set to 60A.

<table>
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<tr>
<th>Label</th>
<th>Nominal bilayer thickness (nm)</th>
<th>Deposition rate</th>
<th>Deposition rate</th>
<th>Bias (PIII)</th>
<th>Number of layers</th>
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<td>AlN (nm/min)</td>
<td>(8 kV, 800Hz)</td>
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<td>28</td>
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<tr>
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<td>23</td>
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<tr>
<td>C4</td>
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<td>ON</td>
<td>14</td>
</tr>
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</table>
Chapter 3 Synthesizing and Characterization Al/AlN nano-structured Coatings

Table 3.2 Summary of deposition conditions for Al and AlN layers

<table>
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<th>N2 Flow rate (sccm)</th>
<th>Pressure (mtorr)</th>
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<td>–</td>
</tr>
<tr>
<td>AlN layer</td>
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<td>35</td>
<td>3.7</td>
<td>5.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

3.2 X-ray Diffraction

The crystal structure and the orientation of Al/AlN nano-structured coatings were characterized by X-ray diffraction. Figure 3.1 (a) shows representative X-ray diffraction patterns for samples L1, L2 and films of Al and AlN prepared using the same deposition conditions. The dominant peak in the Al diffraction pattern was indexed to face centered cubic Al {111} planes at $2\theta = 38.5^\circ$ and the lattice parameter of Al calculated by Bragg’s law [6] was $4.0465\text{Å}$. The AlN film showed a strong reflection {0002} at $2\theta = 35.7^\circ$ and a wide diffraction peak {01\overline{1}0} at about $33.6^\circ$, which is consistent with the hexagonal wurzite phase AlN with a lattice constant of $a = 3.077\text{Å}, c = 5.025\text{Å}$. Both the Al {111} peak and AlN {0002} peak were also observed in the multilayer samples. Figure 3.1(b) shows X-ray diffraction patterns for several of the series C samples. In sample C4 with $\lambda = 30\text{nm}$, the main Al and AlN peaks were clearly visible. As $\lambda$ decreases, both peaks become less pronounced. For example, in the sample C1, only the AlN peak was observed.
Figure 3.1 X-ray diffraction patterns for (a) series L (L1 and L2) samples plus single Al and AlN films prepared without PIII, (b) series C samples prepared using PIII.
3.3 Auger Electron Spectroscopy

Auger depth profiling was performed on a Scanning Auger Nanoprobe VG310F using 3 kV Ar sputtering beam. The Auger depth profiles for three sample sets are shown in figure 3.2. The compositional modulations are clearly resolved in series L samples. There are 14 Al/AlN periods (28 individual layers) in L2 and 4 periods (8 individual layers) in L4 as expected shown in table 3.1. The composition of the AlN layers was found to be stoichiometric by comparison with an AlN standard [7]. Low levels of oxygen were found throughout the coating. In the case of series H samples, completed periods were not as distinct as in series L samples. The level of N was lower than that of Al, especially in sample H4. The composition of the AlN layers was found to be AlN in H1 sample, and Al\textsubscript{x}N with x=1.8 +/-0.2 in sample H4. Series C samples were found to be stoichiometric in the AlN content. No compositional modulations were observed. However, the coatings were found to contain more oxygen, up to 7.5%.
Figure 3.2 Auger depth profile of Al/AlN multilayer in (a) L2 sample (28 layers), (b) L4 sample (8 layers), (c) H1 sample (84 layers), (d) H4 sample (14 layers), (e) C3 sample (28 layers), (f) C4 sample (14 layers).
3.4 Microstructure

3.4.1 Samples L Prepared at Low Deposition Rates

Figure 3.3 shows X-TEM images of the samples in series L. In each image, the silicon substrate is on the bottom left hand side. The individual layers are difficult to resolve in the samples L1 and L2, while clearly seen in sample L4. EELS analysis was performed on these samples and the typical results are shown in figure 3.4. Two plasmon peaks at 15.8eV and 21eV associated with Al and AlN respectively were observed in the low loss EELS spectrum. Figure 3.5 presents a plasmon image of Al taken using a 5eV energy window centred at 15 eV as shown by the box in figure 3.4(a). The distribution of Al is clearly seen in the plasmon map. Plasmon maps were used to determine the spatial location of Al rather than Al elemental maps due to the poor signal to noise ratio of Al elemental maps measured using the Al K edge. This is shown in figure 3.6(a) which is an Al elemental map of the same area of the sample shown in figure 3.5(a) which is an Al plasmon map and demonstrates the improved signal to noise of the plasmon map. In the case of sample prepared with a nominal bilayer thickness of 10nm shown in figure 3.5(a), initially Al and AlN layers were formed which tend to breakup at a thickness of more than approximately 80nm. Figure 3.6 shows an Al elemental map of sample L1 recorded using the Al K edge and N elemental maps recorded near the N L ionisation edge (401eV). In figure 3.6(b) the layer structure was distinct near the substrate and then breaks up beyond 80nm from the substrate, confirming the results of the Al plasmon images in figure 3.5(a).

Selected area electron-diffraction patterns from each multilayer coating are shown as inserts in figure 3.3. Each diffraction pattern was correctly aligned with respect to each image and was indexed as Al and AlN. The \{01\overline{1}0\}_\text{AlN}, \{0002\}_\text{AlN} and \{111\}_\text{Al} diffraction rings were observed in all samples, but these rings were discontinuous, indicating a polycrystalline microstructure. All series L samples exhibited preferred orientation to various degrees in which the AlN \{0002\} or the Al \{111\} planes align parallel to the film surface. The strongest
Figure 3.3 X-TEM images of series L samples (a) L1, $\lambda = 10\text{nm}$; (b) L2, $\lambda = 15\text{nm}$; (c) L3, $\lambda = 30\text{nm}$; (d) L4, $\lambda = 50\text{nm}$. Deposition rate for Al is 8nm/min, for AlN is 3nm/min.
Figure 3.4 Typical low loss EELS spectra taken from different samples of Al/AlN multilayer (a) samples L, (b) samples H, (c) samples C.
Figure 3.5 Plasmon image of Al taken with energy losses at 15 eV with a slit of 5 eV (a) L1, \( \lambda = 10 \text{nm} \), relative thickness \( t/\lambda_p = 0.30 \sim 0.56 \); (b) L2, \( \lambda = 15 \text{nm} \), \( t/\lambda_p = 0.40 \sim 0.65 \); (c) L3, \( \lambda = 30 \text{nm} \), \( t/\lambda_p = 0.45 \sim 0.66 \); (d) L4, \( \lambda = 50 \text{nm} \), \( t/\lambda_p = 0.50 \sim 0.75 \).
Figure 3.6. EFTEM Elemental maps taken with a slit width of 20eV and an exposure time of 10s: (a) Al elemental map of sample L1, $\lambda=10\text{nm}$. Nitrogen elemental maps of: (b) sample L1, $\lambda=10\text{nm}$; (c) L2, $\lambda=15\text{nm}$; (d) L3, $\lambda=30\text{nm}$; (e) L4, $\lambda=50\text{nm}$. 
preferred orientation was observed in sample L2. This type of preferred orientation has been observed previously in AlN films deposited under low stress conditions [8].

Figure 3.7 shows dark field images taken using the partially overlapping (0002)\textsubscript{AlN} and (111)\textsubscript{Al} diffraction spots in samples L1 and L2 (indicated by an arrow). No evidence for epitaxial growth can be seen in these images between Al and AlN layers since there is no continuity of bright regions across the layer interfaces. This is in contrast to Ti/TiN multilayer (see figure 2.2) where epitaxial growth was observed.

A close examination on the sharp interface of sample L4 showed that there was a transition layer about 2nm between Al and AlN layers as shown in figure 3.8. The lattice fringes of the transition layer are different from that of Al and AlN individual layers. It is difficult to determine whether the structure of transition layer is the B1-AlN phase (rocksalt structure) or the zinc-blend AlN phase or something else.

3.4.2 Samples H with high deposition rates

Figure 3.9 shows X-TEM images and diffraction patterns of samples H2, H3 and H4 prepared with higher deposition rates. EELS analysis was also performed on these samples and the results are similar to those prepared at a lower deposition rate (figure 3.4). Two plasmon peaks of Al and AlN at 15.8eV and 21eV respectively were seen in the low loss spectrum, but the intensity of Al plasmon was stronger than that of AlN in figure 3.4(b). Figure 3.10 shows the Al plasmon images of these samples. There is no layer structure in any of these samples indicating that the layer structure breaks down more readily at higher deposition rates. These samples show preferred orientation of the same type but to a lower degree than was observed at lower deposition rates.
Figure 3.7 Dark images taken at the diffraction spots $(0002)_{\text{AlN}} // (111)_{\text{Al}}$ normal to the surface of the film (a) L1, (b) L2.
Figure 3.8 High resolution image shows the transition layer between the Al and AlN layers in sample L4.
Figure 3.9 X-TEM images of series H samples (a) H2, $\lambda=10$nm; (b) H3, $\lambda=15$nm; (c) H4, $\lambda=30$nm.
Figure 3.10 Plasmon images of Al with energy losses at 15eV taken with a slit of 5ev for series H samples (a) H2, $\lambda=10$nm, relative thickness $t/\lambda_p=0.3\sim0.45$; (b) H3, $\lambda=15$nm, $t/\lambda_p=0.45\sim0.65$; (c) H4, $\lambda=30$nm, $t/\lambda_p=0.45\sim0.60$. 
3.4.3 Samples C Prepared with PIII

Figure 3.11 and 3.12 show the X-TEM images and Al maps for the PIII samples C2, C3 and C4. For a nominal bilayer thickness of 15nm (figure 3.11(b) and 3.12(b)), no multilayer structure can be seen, while for a bilayer thickness of 30nm (figure 3.11(c) and 3.12(c)), a multilayer structure is discernable. In this latter case, the interfaces between the layers are not as sharp as samples in series L prepared without PIII. The roughness of interfaces is expected and results from ion bombardment during the PIII pulses as described in chapter 2.5.2, figure 2.8. The Auger result from this sample does not resolve the multilayer structure due to the apparent large variation in interface roughness. The diffraction patterns exhibit preferred orientation of the same type but to a much stronger degree than samples prepared without PIII. No significant epitaxial growth can be seen in the dark film (shown in figure 3.13). The EELS analysis show the intensity of AlN plasmon is stronger than Al (shown in figure 3.4(c)), and different from the results of samples H, indicating that PIII assisted the mobility of N⁺ ions which resulted in more AlN forming.
Figure 3.11 X-TEM images of series C samples (a) C2, $\lambda=10\text{nm}$; (b) C3, $\lambda=15\text{nm}$; (c) C4, $\lambda=30\text{nm}$. 
Figure 3.12 Plasmon images of Al with energy losses at 15eV taken with a slit of 5ev for series C samples (a) C2, $\lambda=10$nm, relative thickness $t/\lambda_p\approx0.65$; (b) C3, $\lambda=15$nm, $t/\lambda_p\approx0.70$; (c) C4, $\lambda=30$nm, $t/\lambda_p\approx0.75$. 
Figure 3.13 Dark images taken at the diffraction spots $(0002)_{\text{AlN}} // (111)_{\text{Al}}$ normal to the surface of the film (a) C2, (b) C3.
3.5 Mechanical Properties

3.5.1 Stress

As discussed in Chapter 2.6.6.2, the stress was determined by measuring the curvature of the silicon wafer before and after deposition and then applying equation (2-15). Figure 3.14 shows the residual stress as a function of \( \lambda \) for all three sample sets. A peak in stress was observed at \( \lambda = 10 \) nm and \( \lambda = 15 \) nm for the samples prepared with PIII (series C) and without PIII (series L and H) respectively. The stress was reduced by using lower deposition rates and was further reduced by the application of the PIII pulses. The lowering of stress as a result of PIII has been observed previously [9]. Generally, the stress in these Al/AlN multilayer films was very low compared with the stress of monolithic AlN deposited under the same conditions, which is 1 GPa [10].

![Figure 3.14](image)

Figure 3.14 The residual stress in Al/AlN multilayer films as a function of bilayer thickness for the three samples sets L (low deposition rate), H (high deposition rate) and C (PIII) as shown in Table 3.1.
3.5.2 Hardness

The hardness was measured using a Hysitron Tribo-Indenter with a standard Berkovich diamond indenter and an indentation load from 200μN-1200μN, load rate was 200μN/s. The penetration depth was chosen as less than 1/10 of the film thickness to avoid substrate effects. For each sample, 25 different points’ indentations were made and the average values of H with standard deviations were obtained.

Hardness was measured on three representative samples for each samples series and the indentation results are shown in figure 3.15(a). These results show no systematic trend with nominal bilayer thickness for samples in each set. Generally hardness in H samples is higher than in L samples at the same nominal bilayer thickness. For comparison purpose, the hardness of single AlN and Al films was also tested; they are 12GPa and 5.56GPa respectively. The hardness values for all the multilayer films fall between these values. There is no evidence for hardness enhancement above that of the constituent materials in these samples.

The hardness as a function of compressive stress is plotted in figure 3.15(b). There may be a relationship between the compressive stress of the film and its hardness. It is expected that films with higher compressive stress will inhibit crack propagation and therefore exhibit higher indentation hardness.
Figure 3.15 (a) Hardness correspondences to nominal bi-layer thickness, (b) Hardness variation as a function of stress.
3.6 Discussion

The X-TEM analysis performed in this study shows that the multilayer structure in Al/AlN breaks down at a critical thickness of the individual layers. For low deposition rates, the breakup occurs at a bilayer thickness of approximately 15nm. At higher deposition rates, more thermal energy is available to assist the mobility of the atoms so that rearrangement of microstructure from layers to islands is encouraged and the formation of larger aggregates is possible.

The increasing stress with decreasing bilayer period can be explained by models based on the Hall-Petch relation [11-12], which predicts that the yield stress will depend on the size of grains which are considered to impede the movement of dislocations. If we assume that the mechanisms for the generation of stress are constant, then observed stress will depend on the yield stress. The Hall-Petch relation [11-12] predicts that the yield stress will increase with decreasing grain size. This model will apply equally well whether the sample contains layers or an agglomerated phase. In many observations of hardness and stress in multilayer structures, the stress does not continue to rise as the period decreases, but instead a maximum is formed [13]. This behaviour could be the result of a stress generation mechanism which increases from zero as the thickness of a layer increases, leading to a maximum in the observed stress [14]. This behaviour is present in our results figure, which shows the formation of a maximum in stress at a bilayer period of approximately 15nm.

The hardness for all three series samples doesn’t seem to follow the Hall-petch relation. There is no enhanced hardness observed in this Al/AlN multilayer system. This result is the same as that reported by other investigators [1-3]. The relationship between the hardness and stress is consistent with the work of others [15] in which the hardness tends to follow the stress trend.

The effect of the PIII pulses on film stress has been well studied [10] where it has been found that the application of high energy PIII pulses decreases the
film stress. This trend is evident in our films with large bilayer periods. As the bilayer thickness decreases, the multilayer structure is increasing affected by the penetration of energetic ions into preceding layers. Assuming that the dominant ion species in the plasma are $N_2^+$ and $Al^+$, SRIM calculations [16] show expected ion ranges in Al metal to be approximately 20nm (shown in figure 3.16). Therefore, significant intermixing between layers is expected to occur at the interfaces between the Al and AlN layers. In the case of thin bilayer thicknesses, the Al regions will be completely nitrogenised as observed both in the TEM and X-ray diffraction results for sample C2 as well as the Auger results for the samples C3 and C4. For samples with thicker Al layers, the intermixing is incomplete and some Al regions remain. The trend of a monotonically increasing stress as the bilayer thickness decreases in the PIII samples is a consequence of the formation of a monolithic AlN film which can sustain a generally higher stress than films containing Al. The maximum seen in films without PIII is not present since the PIII bombardment destroys layers of this thickness by intermixing.

Figure 3.16 SRIM implantation data for
(a) 8keV Al ions into a AlN surface, (b) 4keV N ions into Al surface, (c) 4keV N ions into AlN surface.
The Auger results show a variation in composition between each series of samples. At low deposition rates, the AlN layers are stoichiometric. At higher deposition rates, the AlN layers are somewhat nitrogen deficient. This could be caused by out diffusion of nitrogen at the higher deposition temperature expected in these films. At high deposition rate with PIII, the AlN layers are stoichiometric, too, or somewhat nitrogen rich. This means PIII increased the N$_2^+$ implantation into the films. The relatively high level of oxygen in the samples prepared with PIII can be explained by the formation of reactive sites by ion impacts. An increase in oxygen could also result from increased diffusion in these samples after deposition, due to the increased preferred orientation.

The diffraction patterns showed preferred orientation in both the AlN and Al layers. In our samples the [0002] direction of AlN and the [111] direction of Al lie normal to the plane of the film. Dark field images show no evidence of epitaxy and as expected due to the large mismatch of 9% in the periodicities on the AlN (0002) and Al (111) surfaces. The Al (111) and AlN (0002) surfaces are the lowest energy surfaces for the respective materials. In the absence of epitaxy, the lowest energy interface is expected to be formed by combining the two lowest energy surfaces. This explains the observed preferred orientation.

A transition layer (metastable structure) was observed in interface between individual Al and AlN layers. This stabilization results from minimizing the interfacial energy during the initial stages of layer nucleation. When two materials with different crystal structures that cannot form a coherent interface are deposited in a multilayer structure, one layer may crystallize in a metastable structure that does form a coherent interface with the other layer. A metastable structure with small layer thicknesses (<2 nm) is almost always observed in non-isostructural multilayers. For example, AlN has been stabilized in the rock-salt cubic structure in AlN/TiN[17-19], AlN/VN[19-20], and AlN/NbN nanolayers, where as zinc-blend cubic layers form in AlN/W [21].
3.6.1 Model for Predicting Microstructure

In this section, we develop a simple model\cite{model_reference} that predicts the conditions under which a multilayer film converts to a mixed phase film consisting of a uniform sized spherical phase dispersed in a matrix of another phase (see figure 3.17). We use as a starting point the energy per unit area of the interface between the two phases ($E_{\text{int}}$). We assume that $E_{\text{int}}$ is positive. This will be the case, for example, where the presence of the interface creates unfavourable bonding compared to the cohesive bonds of the separated materials.

For a multilayer film of period $\lambda$, there are two interfaces per period and so the total energy per unit volume of material is

$$E_{\text{multilayer}}^{\text{total}} = \frac{2E_{\text{int}}}{\lambda} \quad (3-1)$$

For a dispersed spherical phase with uniform spheres of radius $r$, the number of spheres per unit volume, $N$, is related to the volume fraction of spheres, $f$, by

$$f = \frac{4\pi r^3 N}{3}$$
$$N = \frac{3f}{4\pi r^3} \quad (3-2)$$

The area of interfaces, $A$, per unit volume is $4\pi r^2 N$, so that

$$A = 4\pi r^2 N = \pi r^2 \frac{3f}{\pi r^3} = \frac{3f}{r}$$

The total interface energy per unit volume in this case is

$$E_{\text{total}}^{\text{spherical}} = \frac{3fE_{\text{int}}}{r} \quad (3-3)$$

The film will break up into spherical particles if

$$E_{\text{total}}^{\text{spherical}} < E_{\text{total}}^{\text{multilayer}} \quad (3-4)$$
Figure 3.17 A diagram showing the microstructure transformation between a multilayer structure and a structure containing an agglomerated phase.

The transformation can only occur, even if it is energetically favourable, provided that there is sufficient mobility to allow the movement of atoms over distances of the order of the sphere radius r. The diffusion length (D) therefore determines the largest radius of spheres that it is possible to form. In our case, the Al is expected to be the diffusing species since Al has a relatively low melting point and AlN is refractory. The model predicts:

- The condition on the radius of the spheres is:
  \[ D > r > \frac{3f\lambda}{2} \]  
  (3-6)

- For a given multilayer period, high growth temperatures will promote the formation of spheres by allowing the mobility required.

- At a given temperature, thin layers will transform to spheres more readily than thick layers because of the limitation on the diffusion length.

The predictions of theory and the results of observations are compared in the diagram of figure 3.18 which shows the radius of the spherical phase as a function of the bilayer period. The line that separates the diagram into a “sphere” region and a “layers” region is calculated from equation (3-5) using \( f = 0.41 \), an average value measured from experiment. The theory predicts that it is possible to observe spheres only in the “sphere” part of the diagram. The
observations of a spherical phase in any of the samples are plotted in figure 3.18 as a solid symbol according to the average radius of agglomerates and the intended bilayer thickness. Series L films show a spherical phase only for the smallest $\lambda$. For larger $\lambda$, diffusion is not sufficient to allow the spherical phase to be accessed. The remaining films in series L therefore show a multilayer structure and are plotted as upward arrows along a line indicating the diffusion limit to the size of the spherical phase.

For series H and C, the diffusion limit is much higher due to the elevated growth temperature that accompanies higher deposition rates. All series H films appear in the “sphere” part of the figure 3.18. Although complicated by implantation effects that may lead to intermixing, series C films also appear in the “sphere” part of the diagram.

![Figure 3.18](image_url)

Figure 3.18 A diagram showing the radius of the spherical phase as a function of the bilayer period for all three series of samples. Also indicated is the diffusion limit for series L showing samples L2, L3 and L4 as upward arrows at the diffusion size limit.
3.7 Conclusions

Al/AlN multilayer structures using two deposition rates with and without PIII were synthesized by the cathodic arc deposition system. Some of the structures were unstable and converted spontaneously into a microstructure without clearly defined layers especially when the synthesis of fine periods was attempted. The stress level in the films without PIII increases as the bilayer period decreases with a maximum at a nominal bilayer thickness of 15 nm after which the stress level falls. PIII reduces the stress except for fine periods.

A model was developed based on energetics and diffusion limited aggregation that is consistent with the observations and predicts when the occurrence of layers or the aggregated phase should occur. High deposition rates or the application of PIII were both found to encourage the transition. It was found that a lower deposition rate was more conductive to the formation of a Al/AlN multilayer structure. A transition layer about 2nm was found between the sharp individual Al and AlN layers in mulatilayer samples prepared at low deposition rates.

PIII assists the mobility of N⁺ ions, increased the energy of N₂⁺ and Al⁺ ions, making them combine easily to form AlN. PIII also modifies the interface structure of Al/AlN multilayer. Diffuse interfaces can be made by applying PIII bias during the growth of a Al/AlN multilayer.

No enhanced hardness was observed in the Al/AlN nano-structured coatings, and the hardness of all films was between that of Al and AlN.
3.8 Bibliography


Chapter 3 Synthesizing and Characterization Al/AlN nano-structured Coatings


Chapter 4

Amorphous Carbon Multilayers Synthesized by Filtered Cathodic Arc Deposition

Amorphous carbon (a-C) is one of the more interesting types of materials which can be deposited by filtered cathodic arc deposition. This is because it can be synthesized with a variety of structures and properties by varying the substrate bias and other experimental conditions. This chapter will explore amorphous carbon multilayers fabricated by filtered cathodic arc deposition system using both DC and, for the first time, periodically varying DC substrate biases. One area of interest is whether the use of substrate biases to generate energetic ions during growth can be used to create diffuse interfaces between layers in the multilayer coating. The microstructure of the coatings is investigated using TEM, with details about local bonding and density provided by EELS. This microstructural information is combined with nano-indentation hardness and stress measurements to explore the physical properties of the coatings.

Some of the work in this chapter has been published in the following paper:

4.0 Introduction

When prepared at low densities of approximately 2 g/cm$^3$, a-C films typically have a low level of intrinsic stress and a structure containing a high proportion of graphite-like ($sp^2$) bonding configurations [1]. At densities in the vicinity of 3 g/cm$^3$, the films are known as tetrahedral a-C (ta-C) and normally contain a high level of compressive stress and have a structure that contains a majority of diamond-like ($sp^3$) bonding. Carbon films with structures ranging from low to high $sp^3$ fraction can be readily formed using energetic condensation methods by varying the substrate bias and hence the energy of the C ions used during synthesis. It is reported [2-3] that ion energy is the single most important parameter in determining properties films deposited by the filtered cathodic arc. The compressive stress and the fraction of $sp^3$ bonding in a-C films increase to a maximum as the carbon ion energy increases to approximately 100 eV and then decrease as the carbon ion energy increases further [2-4]. The average ion energy reaching the substrate can be calculated by the following equation [5]:

$$E_i = qV_b + E_0$$  \hspace{1cm} (4-1)

where $E_i$ is the ion energy reaching the substrate, $q$ is the average ion charge state number, $V_b$ is the absolute value of time-dependent (negative) bias voltage, and $E_0$ is the natural ion energy in the plasma (typically 20eV for cathodic arc sources[4]).

As described in section 2.2.4, a major limitation of a-C films, particularly as the $sp^3$ fraction increases, is that they exhibit high intrinsic compressive stresses which limit the thickness of the films that can be prepared without delaminating. Different techniques have been attempted to reduce this stress, such as incorporating doped elements [6-7], post deposition thermal annealing [8-9] and multilayer design [10]. However, dopant atoms acting as impurities, and annealing leads to graphitization which decreases the hardness and wear...
resistance of the films [11]. Logothetides et al. [12-13] and Sheeja et al. [14-15] reported that soft (sp²-rich) and hard (sp³-rich) alternate layers in a multilayer structure can significantly lower the compressive stress and improve the stability of hard carbon films. Stuber et al. [16] and Zhang et al. [17] designed graded multilayer carbon films with a stepwise DC bias using magnetron sputtering. Other investigations on carbon multilayers [18-20] have shown that multilayers not only reduced the stress, but also lower the wear rate compared to monolithic films and improve the overall hardness. However, this previous work has not investigated in detail the microstructure of the multilayer coatings. In addition, there has been no study of the use of a sinusoidal periodic substrate bias to fabricate graded multilayer carbons.

In this chapter, two types of multilayer carbon films consisting of alternating high (sp³ rich) and low (sp² rich) density carbon layers are investigated. The first type of multilayer consisted of high and low density layers formed by changing the level of DC bias rapidly between two values (non-periodic) during film growth. The second type of multilayer was formed by using a sinusoidal periodic bias during the film growth. Of particular interest is how these different types of bias influence the type of interfaces formed between layers.

Also of interest is whether oriented graphitic layers form within a multilayer structure created by varying ion energy and thus stress. Recent work [21] has shown (see figure 4.1(a)) that high density ta-C forms at room temperature when the film stress is increased above a critical value of 6 ± 1 GPa. In the vicinity of the critical stress, a highly oriented graphite-like material is formed which exhibits low electrical resistance and provides Ohmic contacts to silicon (see figure 4.1(b)). Figure 4.2(a) shows a cross-sectional TEM image of an oriented film. This type of preferred orientation is energetically preferred in a biaxial stress field as shown schematically in figure 4.2(b). It was found that the oriented phase only occurs in the vicinity of the transition stress and when
grown with ion energies above 300 eV. In this chapter, the formation of oriented phases in a multilayer film will also be investigated and compare to this previous work on single layer films.

Figure 4.1 (a) Density as a function of compressive stress for amorphous carbon films prepared with ion energies ranging from 35 to 1000 eV. (b) The through-film resistance per unit thickness as a function of stress. Insets A and B show examples of non-Ohmic and Ohmic current-voltage characteristics, respectively. (a, b) The thin vertical dashed line indicates the predicted transition stress as described in ref [21], with the experimental transition region shown in grey. (From [21])
Figure 4.2(a) Dark field TEM image of an oriented amorphous carbon film. This image was taken with an objective aperture centered on a bright arc corresponding to a graphitic {002} reflection (see arrow in inset A). Inset B shows a high resolution image of the 0.335 nm graphite-like planes aligned perpendicular to the surface of the film. (b) Schematic representation of the arrangement of oriented sp$^2$ sheets energetically preferred in a biaxial stress field indicated by arrows. (From [21])

4.1 Two level a-C multilayer.

(This work was conducted in collaboration with Dr. P.C.T. Ha at the University of Sydney. The a-C multilayer sample synthesis and stress measurements were performed by Dr. P.C.T. Ha. All subsequent analysis including TEM specimen preparation, examination and interpretation was performed by the author)

4.1.1 Experimental Details

The multilayer carbon film was deposited onto silicon (100) wafers with a 99.999% pure graphite target using the Sydney University cathodic arc deposition system described in section 2.5.2. The silicon substrates with a
thickness of 300-400 micrometers were ultrasonic cleaned using ethanol and acetone before inserting into the chamber and mounted on a water-cooled sample holder which could be biased at desired voltage. The depositions were carried out with substrate held at room temperature. The system background pressure was approximately $10^{-5}$ mT. Before deposition, the film was exposed to an argon plasma at a pressure of 20 mT. The argon plasma was generated by substrate pulsed bias of 15 kV with a current of 25 mA and operated for 10 minutes. The carbon film was deposited onto the substrate by triggering the carbon cathode with a typical arc current of 75-80 A. Layers were prepared by varying the negative DC bias between RMS 150 V and RMS 720 V to form 10 layers as outlined in Table 4.1. Figure 4.3 shows the average ion energy calculated using equation (4-1) as a function of deposition time for this sample. Layer J was the first layer deposited onto the substrate and layer A is uppermost layer. A deposition pause of 60 s was taken between each layer. The effects of post-deposition annealing were investigated by cutting a piece of the sample and then annealing it in a vacuum at 600°C for 10 minutes.

![Figure 4.3 A diagram showing average ion energy as a function of deposition time in the sample.](image-url)
Chapter 4 Amorphous Carbon Multilayers Synthesized by Cathodic Arc Deposition

Table 4.1 Details of carbon multilayer prepared by varying the DC bias. The expected stress in each layer determined from the stress versus ion energy curve in reference [22].

<table>
<thead>
<tr>
<th>Layer</th>
<th>Bias (V)</th>
<th>Energy (eV)</th>
<th>Deposition Time (s)</th>
<th>Thickness (nm)</th>
<th>Expected Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>720</td>
<td>740</td>
<td>120</td>
<td>55</td>
<td>3.0</td>
</tr>
<tr>
<td>B</td>
<td>720</td>
<td>740</td>
<td>120</td>
<td>55</td>
<td>3.0</td>
</tr>
<tr>
<td>C</td>
<td>150</td>
<td>170</td>
<td>120</td>
<td>60</td>
<td>8.4</td>
</tr>
<tr>
<td>D</td>
<td>720</td>
<td>740</td>
<td>120</td>
<td>40</td>
<td>3.0</td>
</tr>
<tr>
<td>E</td>
<td>150</td>
<td>170</td>
<td>60</td>
<td>20</td>
<td>8.4</td>
</tr>
<tr>
<td>F</td>
<td>720</td>
<td>740</td>
<td>60</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>G</td>
<td>720</td>
<td>740</td>
<td>60</td>
<td>25</td>
<td>3.0</td>
</tr>
<tr>
<td>H</td>
<td>150</td>
<td>170</td>
<td>60</td>
<td>25</td>
<td>8.4</td>
</tr>
<tr>
<td>I</td>
<td>720</td>
<td>740</td>
<td>60</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>J</td>
<td>150</td>
<td>170</td>
<td>60</td>
<td>35</td>
<td>8.4</td>
</tr>
</tbody>
</table>

4.1.2 Results

4.1.2.1 Stress

The stress of the entire multilayer coating was calculated using Stoney’s expression (see section 2.6.5.1) by measuring the curvature of the silicon wafer before and after deposition and found to be 4.3 GPa. Following annealing, the measured value decreasing slightly to 3.3 GPa. The stress is relatively low compared to a value of approximately 10 GPa for the thin and hard ta-C films studied by Shi et al. [2] and the expected average stress of 5.2 GPa in the layer determined by averaging the stress of all the layers (using results from reference [22]) in proportion to their thickness.

4.1.2.2 Microstructure

Figure 4.4 (a) and (b) shows X-TEM images and diffraction patterns before and after annealing for the multilayer. The images from both samples were found to
be similar. The diffraction patterns showed strong preferred orientation arcs associated with graphite-like regions aligned with their basal planes perpendicular to the plane of the layers. Dark field images taken with an aperture over these arcs shows that these graphite-like regions are scattered through the lower density layers (layers grown with 740 eV ions) in both as deposited and annealed samples (see figure 4.4(c)). High resolution images taken in these layers revealed that the microstructure consists entirely of graphite-like sheets aligned normal to the film surface as shown in figure 4.5(a). The lattice fringes are visible and the spacing was about 3.6 Å measured by the line scanning shown in figure 4.5(b). The \{002\} spacing in defective graphite is often larger than that in crystalline graphite (3.34 Å).

EELS analysis was performed on these samples and typical results are shown in figure 4.6. The layers deposited at 170 eV were found to have a plasmon peak in the vicinity of 30 eV, while layers produced at 740 eV had a lower peak position of around 26 eV as shown in figure 4.6(a). Each carbon K-edge EELS consists of a 1s to $\pi^*$ peak at 285eV, followed by a step at around 289eV as shown in figure 4.6(b). The intensity of the 1s to $\pi^*$ peak at 285eV is much higher for 740 eV layers compared to 150 eV layers. Figure 4.7(a) shows the enlarged image of the multilayer with the surface of the sample is on the left hand side of the image. The layers have been labeled A to J and the thicknesses of the layers are shown in table 4.1. Figure 4.7(b) is an EELS linescan taken horizontally across the image in figure 4.7(a) showing the variation of plasmon peak position with scanning distance in the sample. From this plot it can be seen that the uppermost 20 nm of layer B (deposited at 740 eV) has a higher energy plasmon peak compared to the remainder of this layer. Layer C (deposited at 170 eV) is also found to have a sub-layer of approximately the same thickness with a lower plasmon peak than the remainder of the layer. Layer F and layer G was deposited at 740 eV, but the plasmon energies are different. A closer examination of the enlarged image (figure 4.7(a)) reveals
Figure 4.4 (a) X-TEM image of the multilayer carbon film prepared by varying the ion energy between 740 eV (low density - light) and 170 eV (high density - dark) as shown in table 4.1. (b) and (c) show bright and dark field images for the sample following annealing to 600°C. The dark field image was taken with the objective aperture placed over one of the graphitic {002} arcs in the diffraction pattern of this film (indicated by an arrow).
Figure 4.5 (a) High resolution image shows the fringes of graphite-like aligned normal to the film surface in the low density layers, (b) Line-scan result shows the average distance between the fringes of dotted rectangle in (a).
Figure 4.6 Typical EELS spectra taken from different layers in sample A
(a) low loss spectra, (b) carbon K-edge EELS spectra.
Figure 4.7 (a) A TEM image of the multilayer sample prepared by varying the DC bias according to schedule in table 4.1. The surface of the sample is on the left hand side of the image. (b) An EELS linescan taken horizontally across the image in (a) showing the variation of plasmon peak position and (c) variation of density and fraction of $sp^2$. Relative thickness variation $t/\lambda_p=0.50$--$0.76$. 

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that there are very thin transition layers between the main layers. These are indicated by arrows in figure 4.7(a). As discussed below, these differences are the result of ion implantation effects.

Figure 4.7(c) shows the density (calculated using equation (2-5)) and fraction of $sp^2$ bonded carbon atoms (calculated by using equation (2-6)) as a function of distance. The density varies from 1.95 g/cm$^3$ to 2.8 g/cm$^3$ and the fraction of $sp^2$ varies from 20% to 80%. This plot exhibits an inverse relationship between the density and fraction of $sp^2$. When the fraction of $sp^2$ is high, the density is low. This is expected since higher plasmon peak positions are normally associated with higher $sp^3$ (and hence lower $sp^2$) fractions.

### 4.1.3 Discussion

Stress measurements showed little change, with the measured value decreasing from 4.3 to 3.3 GPa following annealing, which is low compared with single layer ta-C films [2]. A possible explanation for the largely unchanged stress and microstructure structure following annealing arise from other investigations [8-9, 23-24] about thermal stability of ta-C films. They demonstrated that post deposition thermal annealing at 600°C can relieve stress in high density (ta-C) films, while retaining their diamond-like properties. Our results extend the data of Ferrari et al. [9], Friedmann et al. [8, 23] and Anders et al. [24], confirming the thermal stability of ta-C in amorphous multilayer films.

The layers grown at 740 eV contain highly oriented graphitic layers both before and after annealing. As discussed in 4.0, such oriented phases are expected to occur when in layers formed with ion energies above 300 eV and under a biaxial stress in the vicinity of 6 GPa. These conditions arise in the layers grown at 740 eV and not in the layers grown at 170 eV and explain the highly oriented regions observed in the TEM images of 740 eV layers (figure 4.5). Annealing at 600 °C does not appear to greatly alter these highly oriented layers. This is not
surprising since it is known that stable defects such as vacancies in graphite are stable to temperatures up to 1100°C [9,23].

As described in section 4.0, recent work [21] suggests that the oriented graphitic phase is formed in carbon films at room temperature when the stress is $6 \pm 1$ GPa and for ion energies above 300 eV. The fact that such oriented layers were found to occur in the current work at 4.3 GPa suggests that the use of such a high DC bias of 720 V may have significantly heated the sample during deposition. Although not measured \textit{in-situ}, the sample was found to be still warm a few minutes after deposition during sample exchange. These results suggest that depositing films at elevated temperatures and lower stresses can cause similar structural re-arrangements as deposition at room temperature and at higher stress. This effect is well known in ion implantation studies in which elevated substrate temperatures results in “dynamical annealing” in which annealing of the material is aided by the thermal spike which accompanies the passage of an ion through the solid [25].

Depositing a film using 740 eV ions on top of pre-existing film results in some modification of the surface region. This effect can be explained by high energy ions implanting into the surface during the initial stages of film growth. When depositing layer A (740 eV) upon layer B (740 eV) the energetic ions have transformation the top 17 nm of layer B to $sp^3$ rich as showing in figure 4.7(a). This increase in density of the low density amorphous carbon may result from the densification of the surface due to the ion implantation. A similar densification effect has been observed in ion beam irradiated glassy carbon [26], which has a low density and is largely $sp^2$ bonded. The ion bombardment has a different effect on the high density layers as shown near the surface of layer C, which has a lower density surface layer of between 12nm and 17 nm generated during the initial stages of growth of layer B. A reduction in the density of ta-C following ion irradiation has been observed previously [27]. Therefore ion
implantation affects low and high density amorphous carbon differently. Low density amorphous carbon increases in density (and \( sp^3 \) fraction), while high density amorphous carbon (ta-C) decreases in density (and \( sp^3 \) fraction).

The thickness of these sublayers can be estimated using SRIM calculations [28] which uses a Monte Carlo approach to calculate ion ranges. Figure 4.8 shows the expected ion ranges in 2.12 g/cm\(^3\) density C layers assuming that the dominant ion species in the plasma is C\(^+\) [29]. Considering that peak energies of up to 1046 eV are expected for a RMS substrate bias of 720V, the ion range is calculated to be approximately 10 nm. This compares with the thickness of the sub layers measured to be between 12nm and 17 nm. Intermixing between layers is expected to occur at the interfaces between the layers, particularly following the 720V depositions.

![Figure 4.8 SRIM implantation data for C ions with RMS720eV and RMS150eV energy into a carbon layer with different density.](image)

Figure 4.8 SRIM implantation data for C ions with RMS720eV and RMS150eV energy into a carbon layer with different density.
4.2 Graded a-C Multilayers Grown Using a Periodic Bias

In order to modify the interface structure of multilayers and obtain a progressively graded carbon multilayer, in this section a continuously changing bias voltage (in a sinusoidal pattern) was applied to the substrate. As far as the author is aware, this is the first such attempt to synthesis a carbon film with a continuously varying sinusoidal bias.

4.2.1 Creating a Periodic Bias

Figure 4.9 shows the waveform of the periodic bias used. There are three main parameters: amplitude $V_{\text{amplitude}}$, DC offset named $V_{\text{offset}}$ and period $T$. This function can be written as:

$$ V(t) = V_{\text{offset}} + V_{\text{amplitude}} \sin(2\pi t/T) \quad (4.2) $$

The periodic bias $V$ fluctuates continuously between $V_{\text{amplitude}} - V_{\text{offset}}$ and $V_{\text{amplitude}} + V_{\text{offset}}$. The smaller the period, $T$, the more rapidly the bias $V$ fluctuates.

![Diagram of periodic bias](image)

Figure 4.9 A diagram of the periodic bias employed.
4.2.2 Experimental Details

All the samples were prepared using the RMIT filtered cathodic arc deposition system as described in figure 2.7(b). Prior to deposition, the deposition system was evacuated to a vacuum base pressure of $8 \times 10^{-6}$ Torr and then the arc was run for half a minute onto the shutter in order to clean the cathode. The arc current was set to 60A. The other deposition parameters were summarized in table 4.2. Two sets of samples were prepared using the parameters shown in the table 4.3.

<table>
<thead>
<tr>
<th>Arc Current (A)</th>
<th>Arc Voltage (V)</th>
<th>working pressure (mtorr)</th>
<th>Base pressure (mtorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C film</td>
<td>56</td>
<td>28</td>
<td>$5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Table 4.3 Summary of the samples prepared in this work

<table>
<thead>
<tr>
<th>label</th>
<th>$V_{\text{offset}}$ (-eV)</th>
<th>$V_{\text{amplitude}}$ (-eV)</th>
<th>Period T (second)</th>
<th>Deposition time (minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A180_5/A180_10</td>
<td>275</td>
<td>200</td>
<td>180</td>
<td>5/10</td>
</tr>
<tr>
<td>A90_5/A90_10</td>
<td>275</td>
<td>200</td>
<td>90</td>
<td>5/10</td>
</tr>
<tr>
<td>A60_5/A60_10</td>
<td>275</td>
<td>200</td>
<td>60</td>
<td>5/10</td>
</tr>
<tr>
<td>A40_5/A40_10</td>
<td>275</td>
<td>200</td>
<td>40</td>
<td>5/10</td>
</tr>
<tr>
<td>A30_5/A30_10</td>
<td>275</td>
<td>200</td>
<td>30</td>
<td>5/10</td>
</tr>
<tr>
<td>A20_5/A20_10</td>
<td>275</td>
<td>200</td>
<td>20</td>
<td>5/10</td>
</tr>
<tr>
<td>A10_5/A10_10</td>
<td>275</td>
<td>200</td>
<td>10</td>
<td>5/10</td>
</tr>
<tr>
<td>B90_5</td>
<td>150</td>
<td>125</td>
<td>90</td>
<td>5</td>
</tr>
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<td>B60_5</td>
<td>150</td>
<td>125</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>B30_5</td>
<td>150</td>
<td>125</td>
<td>30</td>
<td>5</td>
</tr>
</tbody>
</table>
For sample set A, two samples were prepared for each set of parameters, one for 5 minutes and the other for 10 minutes (about five minutes deposition, pause for five minutes and then a further five minutes deposition). All samples in set B were deposited for 5 minutes. The total thickness of each sample was kept between 100nm and 200nm. The average deposition rate was 0.28nm/s.

### 4.2.3 Results

#### 4.2.3.1 Expected Microstructure Based on the Intrinsic Stress

As discussed above, recent work [21] has found that the stress during growth determines the level of diamond like bonding present in a a-C film. In order to help interpret the microstructure of the periodically varying samples, a relationship between stress and ion energy needs to be found. According to the Davis’s model [30], the stress $\sigma$ is:

$$\sigma = \frac{Y}{1-\nu} \frac{E^{\frac{1}{2}}}{R + jE^{\frac{1}{2}}}$$  \hspace{1cm} (4.3)

where $E$ is the ion energy, $R$ the net depositing flux, $j$ the bombarding flux, $k$ a material-dependent parameter, $Y$ the film material Young’s modulus and $\nu$ the Poisson ratio. Collecting all the free parameters in Davis’s equation in to a single constant $K$, we obtain:

$$\sigma = K \frac{E^{\frac{1}{2}}}{1 + kE^{\frac{1}{2}}}$$  \hspace{1cm} (4.4)

Figure 4.10 shows the stress versus ion energy for single layer carbon films prepared in the same deposition system under identical experimental conditions as those in this study [31]. This data is fitted to the modified Davis’s equation with $K = 1.7$ and $k = 0.0002$ and the fit is shown in figure 4.10. The stress as a
function of deposition time was determined from equation (4-4) and is shown in figure 4.11 for samples in sets A and B. The stress in sample set A follows the bias trend in a similar sinusoidal pattern. However, in set B in which the bias voltage reaches 25 eV which is below the stress maximum, a different waveform is found with a doublet in the stress occurring during the peaks in ion energy.

Figure 4.10 (a)The level of compressive stress in carbon films as a function of ion energy for single layer films prepared in the same deposition system under identical experimental conditions as those in this study [31]. Also shown is a fit to the experimental results using the model of Davis [30] and the range of stresses expected in sample sets A and B.
Figure 4.11 The expected stress variation in samples A and B versus deposition time when the period $T$ equals 90 seconds.

4.2.3.2 Microstructure in Samples A

Figure 4.12 shows X-TEM images for three samples in set A deposited for 10 minutes. A periodic structure can be seen in all the samples. Individual layers can be observed as alternating dark and light phases with intermixing to a various degree between the sub-layers. A distinctly lighter layer, about 12nm thick, was observed in the middle of the film in figure 4.12(a). A selected area diffraction pattern (insert in figure 4.12(a)) shows preferred orientation arcs associated with graphite-like regions aligned with their basal planes perpendicular to the plane of the layers. A dark field image of sample A180_10 taken with an objective aperture positioned over one of the preferred orientation arcs is shown in the figure 4.13(a), illustrating that graphite-like structures oriented with planes perpendicular to the film surface are formed 12 nm thick low density layer in the middle of the film. In addition, lattice fringes of graphite $\{002\}$ planes perpendicular to the film surface can be seen in this layer.
at high resolution as shown in figure 4.13(b) and the spacing of fringes was measured about 3.5 Å by line scanning. No evidence for preferred orientation was observed in other regions of this sample.

Selected area electron-diffraction patterns from the A90_10 and A10_10 are shown as inserts in figure 4.12(b) and (c), respectively, exhibiting typical diffuse ring pattern expected from an amorphous carbon. A dark field image of sample A90_10 was taken with an objective aperture positioned over \{002\} ring perpendicular to the plane of the layers is shown in the figure 4.14(a), revealing a graphitized layer near the surface of multilayer. Again lattice fringes of the graphite \{002\} can be observed in this layer as shown in the high resolution image shown in figure 4.14(b) and measured about 3.5 Å.

Figure 4.15(a) shows the ion energy and corresponding stress variation calculated from equation (4-4) versus deposition time for A180_10. The stress is expected to fluctuate from 5.30 GPa to 11.80 GPa, with an averaged value of 8.2 GPa. Figure 4.15(b) shows an image of this sample aligned with the ion energy and stress curves shown in 4.15(a). An EELS line-scan in the low loss region was collected horizontally across sample A180_10 using a spot size of approximately 5nm in diameter. The variation of plasmon peak position obtained by fitting a Gaussian peak to each low loss spectrum is shown in figure 4.15(c). The plasmon peak position fluctuates with the same period as the stress. The density calculated from the plasmon peak position was found to be approximately 2.95 g/cm\(^3\) during the stress maxima of 12 GPa. This density compares well with that expected for material prepared at high stress from figure 4.1(a). The stress minima (6 GPa) give rise to densities of approximately 2.75 g/cm\(^3\), which is also consistent with the data in figure 4.1(a). The distinctly lighter layer, which was found to contain oriented graphitic material formed near the 5 minute break in deposition, was found to have the lowest density of 2.5 g/cm\(^3\).
Figure 4.16 (a)-(c) shows the variation of ion energy & stress aligned with the image and the plasmon peak position for the initial three cycles of sample A90_10. The plasmon energy fluctuated from 27.2eV to 29.3eV which corresponds to a density fluctuation from 2.3 g/cm³ to 2.7 g/cm³ as shown in figure 4.16(c). The lower density of the high density layers may be the result of thinner layers since it is known that stress takes a little time to build up during film growth [32]. Therefore when layers are very thin, the stress and therefore density will be less than for thicker layers grown under the same conditions.

Figure 4.17 shows a bright filed image and the expected stress fluctuation for sample A10_10. Although layering is evident in the image, the number of layers does not correspond to the number of fluctuations. This may be due to the fact that as the thickness of layers becomes thin, ion implantation causes intermixing between layers. Another possibility is that the bias is changing too rapidly to affect the ion energy leading to a reduction in the number of layers. Some of the lighter layers contained oriented graphitic materials as shown in the high resolution image shown in figure 4.17(c). Due to the relatively large spot size of the available STEM instrumentation in comparison to the layer thicknesses, EELS line-scan were not attempted on this sample.
Figure 4.12 Morphology of samples in set A (a) A180_10; (b) A90_10; (c) A10_10.
Figure 4.13 (a) Dark filed image of sample A180_10. (b) High resolution image in the vicinity of the oriented material shown in (a), line-scan measuring the average distance between the fringes in dotted rectangle.
Figure 4.14 (a) Dark filed image of sample A90_10. (b) High resolution image in the vicinity of the oriented material shown in (a).
Figure 4.15 (a) Ion energy and expected stress as a function of deposition time in A180_10. (b) A TEM image of the multilayer sample A180_10, the surface of the sample is on the right hand side of the image. (c) An EELS line-scan taken horizontally across the image in (b) showing the variation of Plasmon peak position (solid line) and variation of density (dotted line) with scanning distance, relative thickness variation $t/\lambda_p=0.40–0.66$. 

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Figure 4.16 (a) Ion energy and expected stress as a function of deposition time for the initial three cycles in A90_10. (b) A TEM image of the multilayer sample A90_10 for the initial three cycles, the surface of the sample is on the right hand side of the image. (c) An EELS line-scan taken horizontally across the image in (b) showing the variation of plasmon peak position (solid line) and variation of density (dotted line) with scanning distance, relative thickness variation $t/\lambda_p=0.35\sim0.60$. 

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Figure 4.17 (a) Expected stress as a function of deposition time in A10_10. (b) A TEM image of the multilayer sample A10_10, the surface of the sample is on the right hand side of the image. (c) High resolution image showing oriented phases in A10_10.
4.2.3.3 Microstructure in Samples B

X-TEM and EELS analysis were performed on sample B90_5 and the results are shown in figure 4.18. The expected stress varies from 8.25 GPa to 11.8 GPa associated with the ion energy shown in figure 4.18(a). As discussed above, a single stress maximum during each cycle is replaced by a doublet. This doublet is evident in the plasmon peak position and density plots obtained from the EELS linscan taken horizontally across the image in figure 4.18(b). The plasmon energy fluctuates from 27.6 eV to 29.8 eV corresponding to a density variation of 2.4 g/cm\(^3\) to 2.8 g/cm\(^3\). The fact that the doublet in stress causes the expected alteration in structure provides support to the proposition that the level of stress is the most important factor which determines the microstructure of a-C layers. In addition, diffuse diffraction ring was observed in diffraction pattern shown as an insert in figure 4.18(b), indicating there is no oriented graphitic carbon in sample B90_5.

Figure 4.19(a) shows an X-TEM image of sample B30_5. The individual layers are difficult to resolve. The expected stress fluctuation and an enlarged image are shown in figures 4.19(b) and (c). As with sampled A10_10, the difficulty in forming the desired layers may be due to intermixing because of ion implantation.
Figure 4.18(a) Ion energy and expected stress as a function of deposition time in sample B90_5. (b) Image of sample B90_5. (c) An EELS line-scan taken horizontally across the image in (b) showing the variation of plasmon peak position (solid line) and variation of density (dotted line) with scanning distance, relative thickness variation $t/\lambda_p=0.50~0.70$. 

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Figure 4.19 (a) TEM image of sample B30_5. (b) Expected stress variation as a function of deposition time. (c) Enlarged image of sample B30_5.
4.2.3.4 Stress

The variation in residual intrinsic stress for samples in set A plotted against the period T of substrate bias is shown in figure 4.20. Since the stress was measured at the end of the deposition, it represents the average stress of the entire coating. The samples in set A show an increase in stress from 6.5 GPa to 8.5 GPa as the period T increases from 10 to 180 s. This increase in average coating stress may be the result of increasing layer thicknesses which allow the level of stress to build up to that of thick films prepared under the same conditions of ion energy. The expected average stress in samples A from the waveform shown in figure 4.11 is 8.22 GPa, close to the average stress measured for the longest periods and thicker layers.

![Figure 4.20 Variation of compressive stress as a function of period T for samples in set A.](image-url)
4.2.3.5 Hardness

Figure 4.21(a) shows the nanoindentation hardness and elastic modulus as a function of the period T for samples in set A. In order to compare the relative hardness and moduli of different films, the hardness and elastic modulus were measured at a contact depth of 23.5% of the film thickness. It can be seen from figure 4.21 that the hardness at about 40GPa for periods of 30 to 40 s and then decreases slightly. A similar trend was observed for the Young’s modulus. The hardness of the single layer a-C film prepared at -400V bias was found to be 36.4GPa. The hardness and Young’s modulus of silicon are approximately 12Gpa and 170Gpa, respectively [33]. Therefore, the carbon multilayers have increased the hardness and elastic modulus of the silicon substrate.

Figure 4.21(b) shows the variation of hardness as a function of stress. The hardness increases as stress increases. Increases in hardness are often observed in coatings as the level of compressive stress increases since compressive stress would tend to inhibit crack propagation.
Figure 4.21 (a) Variation of hardness and elastic modulus as a function of bias period T in samples A and hardness of a-C single film prepared at -400V substrate bias. (b) Hardness variation as a function of stress.
4.2.4 Discussion

The X-TEM analysis performed in this section shows that multilayer carbon films with graded interfaces can be prepared using a periodic bias. A graded interface is formed due to the variation in carbon ion energy leading to stress gradients which results in density gradients. The number and density of the layers were found to correlate well with that expected from the variation in stress calculated from Davis model which relates ion energy with stress. This result supports the proposition that the stress under which a carbon film is formed is the most important factor determining its microstructure. For the samples prepared using the smallest periods, the number of layers is lower than expected due to the thin layers and the effect of ion implantation.

There is pronounced light layer which is about 12nm width in the middle of A180_10 sample, indicating that the break in deposition has an effect on the microstructure. This effect appears to decrease the density (or $sp^2$ fraction) of this part of film. The most likely cause for this layer is surface relaxation. This phenomenon also occurs in sample A90_10 and A10_10, A light layer was observed during deposition pause (see figure 4.12(b) and figure 4.17(b)).

The results of this section demonstrate that preferred orientation does not always occur in multilayer films with a stress of 6 ± 1 GPa and for ion energies greater than 300eV, as observed previously for single layer films [21]. The difference in the films presented here is that the ion energy is continuously changing which is likely to have an effect on the microstructure of the film. These results indicated that it may take time at a given set of conditions for the oriented phase to form. The tendency for the oriented phase to be observed following breaks in the deposition supports this view.

The expected average stress in the samples in set A is 8.2 GPa. However, the measured stress for the samples in set A was lower than the expected average
stress, except in the case of samples prepared for the longest period. The lower than expected stress may result either from the fact that for thin a-C layers, the level of stress will not have had time to build up. Puchert et al. [32] measured the stress as function of the thin film thickness \textit{in-situ} and found some time is required for stress to build up during film growth before the level saturated. Therefore lower stresses would be expected for the samples in set A with thin layers. Another possibility for the lower than expected stresses is the effective density of interfaces in these samples. Ruud et al. [34] and Awano et al. [35] discussed the interface stresses caused by surface free energy in metallic multilayers and proposed that the interface stresses are important influences on the total residual stress of a multilayered film. The introduction of more interfaces in multilayers prepared with more periods may reduce the residual stress of the coating.

No enhancement in hardness compared with single ta-C film was observed in the multilayer films. As the hardness of the films is related to their \( \text{sp}^3 \) fraction [36], the hardness values would be largely dependent on the number of ta-C layers. The depth of penetration of the indents would be expected to have an effect on the hardness measurements and the hard ta-C sub-layer is not always the surface layer for shallow indents. The uppermost layers for all the samples are soft or hard depending on the periodic bias which begins at the same voltage, but ends at a different voltage for each of the samples, thus influencing the hardness measurements. Therefore the sharp drop in hardness which occurs in sample A90_10 can be explained by the soft outmost layer.

\textbf{4.3 Conclusions}

The structure and annealing properties of a multilayer carbon film consisting of low and high density layers deposited by changing the growth energy between 170eV and 740 eV has been investigated. Annealing did not significantly alter
the structure and only marginally reduced the stress. The structure of the high density (ta-C) layers was found to be largely unchanged by the annealing. These results demonstrated thermal stability of ta-C in a-C multilayers. It was found that the use of energetic ion species to grow layers results in interface modification due to ion bombardment. This modification was found to be different depending on whether the layer being implanted has a low or high density. Low density layers where found to increase in density, while high density layers showed an opposite effect by decreasing in density.

It was also shown that it is possible to deposit multilayers of hard and soft amorphous carbon with gradual interfaces by applying a bias in a sinusoidal pattern using a filtered cathodic arc deposition system. The stress variation across the graded multilayer films was lower than that expected, except for the longer periods. The increasing stress with increasing period T of bias can be explained by the time required for stress to build up and the density of interfaces. No significant enhanced hardness was observed. Hardness increases as stress increases in these graded multilayer carbons. Deposition pauses during film growth can cause surface relaxation, which results in oriented graphic layers.

4.4 Bibliography


31. See EPAPS Document No. E-PRLTAO-100-055817 for a graph of the stress verse ion curve. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.


Chapter 5

Metal/a-C Nano-structured Coatings Prepared by Unbalanced Magnetron Sputtering

This chapter explores the microstructure of metal/a-C nano-structured coatings. Two sets of metal/a-C nano-structured coatings are fabricated using an unbalanced magnetron sputtering deposition system. Cross-sectional transmission electron microscopy, Raman spectrum and Auger depth profiling are used to investigate the microstructure of the films.

5.0 Introduction

As described in section 2.2.4 and section 4.0, the use of multilayers can be used as an effective method to reduce stress in amorphous carbon films. It is also of considerable interest to investigate extremely heterogeneous multilayer systems comprising of amorphous carbon films with much softer metallic films. The combination of amorphous and crystalline layers has been shown [1-4] to not only increase the hardness but also hinder crack propagation across the interfaces of the multilayer. This leads to a toughening of the multilayer system and to a reduction in wear. Additionally, metallic layers can also be used to increase the adhesive strength of the multilayer coating to the substrate and thereby reduce the possibility of delamination. However, there is very little information in the literature on multilayers composed of a crystalline and an amorphous carbon phase. The only reported metal/carbon multilayer systems include Ti/C [5], a-C/Mo [6], a-C/W [6-7], Cr/a-C [8-9] and Al/C [10]. These
multilayers have shown significant advantages over their monolithic a-C films. In a previous study, Al/C multilayers synthesized by the laser-arc technique showed an increase in adhesion and a decrease in the tribological properties with increasing aluminium content [10]. However, no investigation was carried out on the microstructure of the layers.

The aim of the present study is to combine hydrogen-free amorphous carbon coatings with a soft aluminium layers into a nano-structured coating with the goal of increasing the total coating thickness by reducing the internal stress while retaining good mechanical properties. This study will also explore whether multilayer coatings can be successfully made by rotating a specimen in between two magnetron sputtering sources containing Al and C. If successful, this method for producing multilayers may be more amenable to the production of coatings industrially where magnetron sputtering is often employed.

5.1 Experimental Details

The Al/a-C nano-structured films were deposited using an unbalanced magnetron sputtering system equipped with a vacuum chamber 80 cm in diameter and 120 cm in height. Figure 5.1 shows a cross-sectional diagram of the chamber, which depicts four strips of magnetron sputtering targets (720×120mm) and two IBS (Ion Beam Sources) around the wall of vacuum chamber. Two metallic targets were located on the left side and two graphite targets on the right side. Si wafers, ultrasonically cleaned in acetone and alcohol, were used as the substrates. The samples were placed on a rotary sample holder in the centre of vacuum chamber. Prior to deposition, the chamber was evacuated down to 2×10⁻³ Pa and pure Ar (99.99%) was leaked into the chamber to achieve a pressure of 3×10⁻¹ Pa. Each substrate was presputtered in a pure argon atmosphere with a negative bias voltage of 800V for about 10 minutes and all targets were cleaned by Ar⁺ ion etching for 10 minutes.
before deposition was conducted. The distance between the substrates and
targets was about 10 cm. The sample holder was equipped with a heater and
this allowed all samples to be deposited at a temperature of 150 °C.

In this work, two sets of Al/a-C nano-structured coating samples were prepared
labelled series R and series S as listed in table 5.1. For samples in set R used to
evaluate the sputter deposition system, Ar gas was injected at a flow rate of 28
sccm. Powers of 1.25kW and 14kW were applied to the two Al targets and two
carbon targets, respectively. Negative pulsed biases of 100V and 500V, 40kHz
were applied to the substrate during the deposition (shown in table 5.1). In set
R, either an Al layer or an a-C layer was deposited by switching on either the Al
or graphite targets. In all cases, a thicker Al layer was deposited as the first
layer on the Si substrate. The total thickness of each coating was about 240nm.

For samples in set S, a shutter was placed in the middle of the vacuum chamber,
separating the chamber into two parts (see figure 5.1). This allowed four targets
(one Al, one Cr and two graphite) to be run simultaneously so that the Al was
deposited as the substrate rotated past the left side of the chamber and the a-C
was deposited as the substrate rotated past the right side of the chamber. The
Cr target was only used during the initial 6 minutes of deposition in order to
produce a Cr/Al interface layer. DC Powers of 270V and 200V were applied to
the Al and Cr targets respectively. A pulse power of 5kW was applied to two
carbon targets. In these samples, the nominal thickness of each layer was
controlled by changing the rotation speed of the sample holder. Three different
rotation speeds were used: 1rpm, 3rpm and 5rpm. The total thickness of each
sample was about 450nm. The deposition conditions for both sample sets are
summarized in tables 5.2 and 5.3.
Figure 5.1 Schematic diagram of the mid-frequency magnetron sputtering system, four targets around the chamber wall; dotted line represents the removable shutter only employed in preparing samples S (top-view).

Table 5.1 Summary of the samples prepared in this work

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</tr>
</tbody>
</table>
5.2 Results I: The Microstructure of Samples in Set R

5.2.1 Auger Electron Spectroscopy

The Auger depth profiles for samples in set R are shown in figure 5.2. The compositional modulations were clear. The profiles show 12 periods in R1, 8 periods in R2, 6 periods in R3 and 5 periods in R4 as expected. All the samples were found to contain some oxygen (approximately 5%) due to the low base vacuum used in this deposition system. Due to the limited depth resolution inherent in sputter depth profiles, the maximum and minimum elemental concentrations in each layer are not resolved. For samples R2, R3 and R4 there was also a considerable amount of Fe found in the samples, particularly in the Al layers. This source of this Fe is re-sputtering due to the high substrate bias as discussed below.
Figure 5.2 Auger depth profiles of (a) R1, (b) R2, (c) R3, (d) R4.

C     ,  A l      ,  F e     ,  O     ,  S i     

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5.2.2 X-Ray Diffraction

Figure 5.3 shows the X-Ray diffraction spectra for samples R1, R2, R3 and Si substrate. Besides the peak of Si in the diffraction spectra, the dominant peak in the R1 was indexed to face centred cubic Al \{111\} planes at $2\theta = 38.5^\circ$ and the dominant peaks in the R2 and R3 were indexed to body centred cubic Fe \{110\} planes at $2\theta = 43.8^\circ$. The lattice parameter of Fe calculated by Bragg’s law was 2.920Å. Interestingly the dispersed Fe in the films formed the body centred cubic $\alpha$-Fe phase which is a substitution solid solution with a solubility of 0.0218 wt. % C in Fe-C alloys at the room temperature.

![X-Ray diffraction spectra from samples and Si substrate.](image)

5.2.3 Transmission Electron Microscopy

Figure 5.4 shows X-TEM images of the samples in set R. Multilayer structures were visible and the individual layers are very clear. No columnar structures and epitaxial growth were observed in these films. In sample R1, the first Al layer can be seen which appears to have a polycrystalline microstructure. The second layer was $a$-C layer which has a wrinkled structure and found to have
preferred orientation deduced from the diffraction shown as an insert in figure 5.4(a). The preferred orientation is seen in the strong arcs in the vicinity of the graphite \{002\} reflections. As was the case in the carbon/carbon multilayers in chapter 4, the arcs reveal the presence of strong preferred orientation of the graphite-like layered structures with their planes aligned perpendicular to the film surface. The \{002\} graphitic planes separated by about 0.35nm are clearly seen in high-resolution image shown in figure 5.5(a) and the interface between the Al and a-C phases appears relatively sharp indicated by the line. Dark field images were taken with an objective aperture positioned over one of the preferred orientation arcs was shown in figure 5.5(b), showing that the carbon layers contain oriented graphitic carbon.

In samples R2, R3 and R4, the first layer is an Al layer where the type Al microstructure is not clear. The second layer was a carbon layer which was found to have an obvious lamellar-like appearance or columnar-like structure (shown in figure 5.4 (b)-(d)). When the second Al (α-Fe) layer was deposited, the columnar-like growth structure stopped. The diffraction patterns in figure 5.4(b) and figure 5.4(c) show a strong sharp ring expected from iron, which has a d-spacing of 2.07–2.14Å corresponding to body centred cubic α-Fe phase \{110\}. It is obvious that the strong sharp ring is different from the diffuse ring produced by amorphous carbon shown in figure 4.7, chapter 4. Dark film taken with an objective aperture positioned over the \{110\} α-Fe strong diffraction ring was shown in figure 5.6(a). Figure 5.6(b) shows the bright film image taken at the same region for comparison in sample R2. It is clear that iron rich layers have formed with the face centred cubic α-Fe structure. Disordered and ordered fringes from graphitic \{002\} layers were observed in high resolution image in figure 5.6(c) in sample R2 and the interface between the Al(α-Fe) layer and a-C (α-Fe) phases appears relatively sharp indicated by the line.
Figure 5.4 X-TEM images of series R samples (a) R1, $\lambda = 20$nm; (b) R2, $\lambda = 30$nm, (c) R3, $\lambda = 40$nm (d) R4, $\lambda = 50$nm.
Figure 5.5 (a) HREM image of sample R1 - dotted lines indicated the interface between the Al layer and a-C layer, showing ordered fringes from graphitic {002} layers. (b) Dark field image taken from one of the sharp {002} diffraction arcs seen in this sample.
Figure 5.6 (a) Dark film taken over the \{110\}_α-Fe diffraction ring. (b) Bright film taken at the same region as (a). (c) High resolution image in sample R2- dotted lines indicated the interface between the Al layer and a-C layer, showing disordered and ordered fringes from graphitic \{002\} layers.
EELS analysis was performed on several of the samples in set R. Figure 5.7(a) shows a low loss EELS spectrum from an area of the coatings which included both Al and C layers in set R. The broad peak is a superposition of the two most intense plasmon peaks for Al (at approximately 16 eV) and a-C (at approximately 25 eV). These two plasmon peaks have been fitted to the spectrum in figure 5.7(a) shown as dotted lines. An EELS line scan was taken from the surface of the sample to the underlying substrate and then fitted with two plasmon peaks. The results are shown in figure 5.7(b) and 5.7(c) the variation of the intensity of each plasmon as the beam scans through the coating exhibiting the 12 periods in sample R1 and 6 periods in sample R3.

Figure 5.8 shows elemental maps of C and Al in sample R1, exhibiting the distribution of elemental Al and C in this coating. Individual Al layers are very clear, while carbon layer is visible and it seems that carbon dispersed through the whole film. This result is consistence with Auger spectrum in sample R1, where the amount of carbon is much high than Al.

Figure 5.9(a) and 5.9(b) presents plasmon images of Al and C, taken using a 5eV energy window centred at 16 eV and 25eV, respectively in sample R2. Figure 5.9(c) and 5.9(d) show the elemental maps of C and Fe in sample R2. It can be seen Fe exists in the whole film. All the images clearly indicated the multilayer structure in sample R2.

The elemental maps of Fe and C in sample R3 are shown in figure 5.10, illustrating 6 layers of a-C and the presence of Fe throughout the whole film. The Plasmon image of Al was also taken at 16eV with a slit 5eV. These EELS maps are consistence with Auger spectra which also shown that Fe was present throughout the coating. The origin of Fe in samples R2, R3 and R4 is discussed below.
Figure 5.7 (a) A typical low loss energy spectrum from set R. Variation of the intensity of Gaussians fit for both Al and C in low loss spectra as the beam scans through the coating in (b) R1, (c) R3.
Figure 5.8 EFTEM images of sample R1 with a slit width of 20eV and an exposure time of 10s (a) Al elemental map (Al-L$_{23}$), (b) C elemental map (C-K).
Figure 5.9 EFTEM images of sample R2 (a) Plasmon image of Al, taken at 17eV with a slit of 5eV, (b) Plasmon image of C, taken at 26eV with a slit of 5eV, (c) C elemental map (C-K) with a slit width of 20eV and an exposure time of 10s, (d) Fe elemental map (Fe-L) with a slit width of 20eV and an exposure time of 10s.
Figure 5.10 EFTEM images of sample R3 (a) Plasmon image of Al taken at 16eV with a slit of 5eV, (b) C elemental map (C-K) with a slit width of 20eV and an exposure time of 10s, (c) Fe elemental map (Fe-L) with a slit width of 20eV and an exposure time of 10s.
5.3 Results II: The Microstructure of Samples in Set S

5.3.1 Auger Electron Spectroscopy

The Auger depth profile for sample S3 is shown in figure 5.11. No compositional modulation was observed in this sample which would indicate a multilayer structure. The amount of Al was much higher than that of C, indicating that the Al/C coating is dominated by Al. High levels of chromium were found in the transition layer near the substrate as expected from the deposition plan outlined above. As with samples in set R, the coating was found to contain a high proportion of oxygen due to the low base vacuum of the chamber during the deposition.

![Auger depth profile of sample S2 with 3rpm.](image.png)
5.3.2 Microstructure

Figure 5.12 presents the TEM images of samples in set S. The Cr layer between the silicon substrate and the Al/C coating can be clearly seen. For all three rotation speeds, the Al/C coating appears to contain a largely nano-composite microstructure, not a multilayer as intended. A closer examination of the initial stages of film growth of the Al/C coatings is shown on the right hand side of each image in figure 5.12. A layered structure is visible immediately on top of the Cr interface layer, which eventually breaks up as the coating becomes thicker. The bilayer thickness in the region indicated by a circle decreased from 20nm to 8.7nm in figure 5.12(a), about 6nm in figure 5.12(b), and less than 4nm in figure 5.12(c). This decrease in thickness is consistent with the increasing rotation speeds.

The diffraction patterns shown as inserts in figure 5.12 reveal discontinuous rings indicating the presence of a polycrystalline microstructure. The \( d \)-spacing of the first three rings of the SAED pattern was found to be 2.33 Å, 2.02 Å, and 1.43 Å, corresponding to the \{111\}, \{200\}, and \{220\} reflections of faced-cubic crystal Al, respectively. It is seen that the intensity of diffraction of Al becomes less as the sample holder rotation speed increases, indicating that the crystallinity of the Al decreases as the sample holder rotation speed increases. Dark field images taken from the Al (111) reflection are shown in figure 5.13 for the 1 and 5 rpm samples. The average Al grain size becomes finer with a size of approximately 8~25nm in figure 5.13(a) and 3~4 nm in figure 5.13(b) as the sample holder rotation speed increases.
Figure 5.12 Cross-sectional TEM images of samples in set S (a) S1, 1rpm; (b) S2, 3rpm; (c) S3, 5rpm. The insert in the top right hand corner of each image is a selected area diffraction pattern from each Al/C film. The images on the left are enlargements of the initial stages of Al/C film growth.
5.3.2 Raman Spectroscopy

In order to characterise the nature of the carbon in the Al/C coatings, Raman spectroscopy was performed. As discussed in chapter 2.6.3, the Raman spectrum from disordered carbon are characterised by peaks centred on 1580 cm\(^{-1}\) (known as the G-band) with another peak at around 1350 cm\(^{-1}\) (known as the D-band). The intensity ratio of the G- and D- bands, peak positions and widths have been commonly used to evaluate the average crystalline size of any graphitic material present [11-13].
The Raman spectra for each sample in set S are shown in figure 5.14. Also shown are fits to the two main lines using a lorenzian line shape for each peak. Table 5.4 shows the results of the fits for each sample. As the rotation speed increases, the G-band shifts to higher wave numbers and the D-band becomes sharper. The peak intensity of the D-band for the 1 rpm sample is higher than that of the G-band in the 3 rpm sample. These changes correspond to the development of a more ordered graphitic microstructure in the 3 rpm sample as shown by the similarity of this Raman spectrum with that of glassy carbon (see figure 2.14 in chapter 2), which has good in-plane graphitic order. The FWHM of the G peak decreases as the rotation speed increases indicating that the in-plane graphitic order within the films increases as the rotation speed increases. At the same time, the relative intensity of the D- and G-bands, decreases as the graphitic crystalline size increases at high rotation speeds.

<table>
<thead>
<tr>
<th>Samples</th>
<th>D-band fit</th>
<th>G-band fit</th>
<th>I_D/I_G</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Position(cm⁻¹)</td>
<td>Intensity</td>
<td>FWHM</td>
</tr>
<tr>
<td>S1</td>
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<td>36686</td>
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</tr>
<tr>
<td>S2</td>
<td>1339</td>
<td>41107</td>
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</tr>
<tr>
<td>S3</td>
<td>1330</td>
<td>7890</td>
<td>2.22</td>
</tr>
</tbody>
</table>
Figure 5.14 Raman spectra of samples in set S
(a) S1, 1rpm, (b) S2, 3rpm, (c) S3, 5rpm
5.4 Discussion

Magnetron sputtering was used to prepare nano-structured Al/a-C coatings. The samples prepared by switching on either Al or C targets to produce layers (set R) were found to successfully produce multilayer coatings with layer thicknesses down to 10 nm. However, both the Auger profiles and electron microscopy revealed that Fe was present in samples of the R series for bilayer thickness above 20 nm and prepared using high substrate bias (-500 eV). This impurity Fe appears to increase towards the surface of the sample (lower sputter times). The origin of this Fe is believed to be the contamination of the Al targets as a result of sputtering from the substrate holder which was made of iron due to the high bias. When preparing carbon layers, Al targets were switched off, iron and carbon were also deposited on the surface of Al target beside the substrate; when the Al targets were switched on, iron was re-sputtered from the surface of Al target and deposited on the substrate with Al. Target contamination will be less for the sample R1 due to the low substrate bias (-100 V) and the shortest running time, which may explain why no Fe was found in the sample with the thinnest layers (R1). Evidence for this proposition is provided by the EDS data shown in figure 5.15. A fresh target appears to be free of Fe as shown in figure 5.14(a). A target which was taken from the system after samples were run showed clear evidence of Fe. For samples in the S series no Fe was found. This may result from two factors: one is due to fact that the Al target was always switched on so that iron is unlikely to settle on the surface of the Al target, another possibility is the substrate bias was -100 V, lower than that in samples R, leading to little or no sputtering from substrate holder.

The X-TEM analysis performed in this study shows that the multilayer structures were seen in all samples in set R. A columnar-like structure within the a-C layers was observed except for the sample with the smallest bi-layer thickness. Similar columnar-like structure was explained previously by low
compressive stresses in a-C multilayers [14]. Low stresses in the coatings prepared in this work may arise from the relaxation of metallic layers. Columnar morphology in the a-C layers found in this work is in contrast to what was observed in a-C/Cr multilayers [4-5], where the columnar structure was found in the metallic Cr layers and a-C layers were introduced to inhibit the columnar growth.

The samples prepared by using the rotation of the sample holder in an attempt to form multilayers (set S) were found to be successful only during the initial stages of film growth. After this initial layering nanocomposites were formed. This phenomenon is very similar to the Al/AlN multilayer system outlined in chapter 3 in which instead of layers, nanocomposites tended to form. Nanocomposite structures will form when surface mobility of the deposited species is large, so atoms can agglomerate to form islands instead of multilayers.
Chapter 5 Metal/a-C Nano-structured Coatings Prepared by Unbalanced magnetron Sputtering

The microstructure of the nanocomposite samples prepared in set S was found to have some interesting trends with specimen rotation speed. As the substrate holder speed increases, the Al crystallite becomes finer and the graphitic regions become more ordered. The smaller Al crystallites result from the fact that the substrate spends less time in front of the Al target at higher rotation speeds. Less Al deposition would result in smaller Al regions forming in the coating. The better in-plane graphitic order within the coatings, as measured using Raman spectroscopy, at higher rotation speeds are possibility the result of the finer Al regions which allow more extended graphitic layers to form.

5.5 Conclusions

This chapter presents results from attempts to prepare Al/a-C nano-structured coatings using an unbalanced sputtering system by switching the targets on or off alternatively. In some cases, well defined layer structures were produced, however Fe contamination was found to occur in some cases due to high substrate biases.

The a-C layer in the Al/a-C coating with the smallest bi-layer thickness prepared using low substrate bias (-100eV) was found to have preferred orientation with graphitic {002} planes aligned perpendicular to the film surface and no Fe contamination through the entire coating. For samples with larger bi-layer thicknesses, multilayers seemed to form, however, Fe contamination was found throughout the coating due to the high substrate bias resulting in the contamination of the Al targets with Fe sputtering off the substrate holder. So an appropriate substrate bias (normally of -100eV) should be used to prevent Fe contamination of Al target when the unbalanced magnetron sputtering system is used to prepare the coatings. This result again highlights the need to conduct detailed microstructural characterisation of nano-structured coatings so that unforseen changes in microstructure and composition can be identified.
An attempt to form multilayers using a rotating substrate holder between two types of sputter sources was unsuccessful. Although layers were formed initially, the coatings were found to mainly nanocomposites. The formation of nanocomposites is expected when the mobility of the depositing species is large so that agglomeration occurs.

5.6 Bibliography


Chapter 6

Conclusions and Future Work

6.1 Conclusions

This thesis explored nano-structured multilayers of aluminium/aluminium nitride (Al/AlN), amorphous carbon/amorphous carbon (a-C/a-C) and aluminium/carbon (Al/C) with different techniques for deposition, namely cathodic arc and magnesium sputtering. Depending on the preparation conditions, these techniques produce very different outcomes in both microstructure and mechanical properties. In particular, employing a substrate bias to vary the energy of the ions participating in film growth was found to significantly influence film microstructure and allowed multilayers to be formed with either sharp or diffuse interfaces. A key requirement for this work was detailed characterisation of the microstructure so that the effects of variations in the deposition parameters could be determined. Therefore the film microstructure was analysed using a range of characterisation techniques and to determine any relationships between the microstructure and the mechanical properties.

Filtered cathodic arc deposition was used to prepare Al/AlN nano-structured coatings using different deposition rates. It was found that multilayers were not formed as expected for all preparation conditions. A model was developed based on energetics and diffusion limited aggregation that is consistent with the observations and predicts when the occurrence of layers or the aggregated phase should occur. High deposition rates or the application of a pulsed substrate bias (PIII) were both found to encourage the transition. A lower deposition rate may be more conductive to the formation of Al/AlN multilayer structure. In the case of multilayer structures, a transition layer about 2nm...
was found between the sharp individual Al and AlN layers. This thesis found no evidence for enhanced hardness in the Al/AlN nano-structured coatings as a function of feature size. The hardness of the Al/AlN films was found to be between that of single layer Al and AlN films. There was some evidence for a relationship between hardness and intrinsic compressive stress in Al/AlN nano-structured coatings. This would be consistent with the proposition that films with higher compressive stresses are harder as a result of the inhibition of crack propagation.

Multilayers of a-C with sharp and graded interfaces were synthesized by cathodic arc deposition using different substrate biases to control the depositing ion energy. For high and low density a-C multilayers prepared using a DC bias, annealing to 600°C did not significantly alter the structure and only marginally reduced the stress. The structure of the high density tetrahedral a-C or ta-C layers were found to be largely unchanged by the annealing. These results extend the previous data, confirming the thermal stability of ta-C in multilayers. For a-C multilayers synthesized using a periodic bias, the microstructure was found to correlate with ion energy and the expected stress based on stress versus ion energy measurements and theoretical models. This result supports the proposition that the stress under which a carbon film is formed is the most important factor determining its microstructure. Interface modification in these two types of a-C multilayers results from the combination of effects, including interdiffusion between layers, relaxation at surfaces or pauses in deposition, and ion implantation.

Unbalanced magnetron sputtering was used to deposit Al/a-C multilayers with well-defined layer structures by switching the targets on or off alternatively. However, Fe contamination was found throughout many of the coatings. The Fe appears to have resulted from sputtering off the target holder onto the Al targets. An attempt to from multilayers using a rotating substrate holder between two types of sputter sources was unsuccessful. Although layers were formed initially, the coatings were found to mainly nanocomposites. The
formation of nanocomposites is expected when the mobility of the depositing species is large so that agglomeration occurs.

The main findings of this thesis are that:

- It is essential to conduct detailed microstructural characterisation of nano-structured coatings in order to gain full understanding of how they form and behave. Many authors present work in which multilayer structures are assumed and hardness and other properties are related to bi-layer thickness. It is clear from this work, that one cannot assume that multilayers will form in all cases and the microstructure needs to be checked prior to making any statements on the relationship between structure and properties.

- A model was developed based on energetics and diffusion limited aggregation that is consistent with the observations in the Al/AlN system and predicts when the occurrence of layers or the aggregated phase should occur. This model is equally applicable to other systems and can be used by investigators to help explain why a nanocomposite forms instead of a multilayer under certain conditions.

- To author's knowledge, this thesis presented the first attempt to synthesis a carbon film with a continuously varying DC bias. a-C multilayers with graded interfaces were synthesized using this periodic bias. The use of a periodic bias confirmed the proposition that the stress under which a carbon film is formed is the most important factor determining its microstructure.

- This thesis found no evidence for hardening enhancements based on multilayer period or feature size. Instead, the only relationship which could be found was some evidence that hardness is proportional to the compressive stress of the film.

- This research program showed that it is possible to produce different interface types (sharp and diffuse) by varying the energy of the
depositing species using different substrate biases in a cathodic arc deposition system. This method is reproducible. The ability to make multilayers with graded interfaces may be important for other applications such as optical coatings and bioimplants.

### 6.2 Further Work

From the conclusions described above, some ideas and suggestions have arisen. Possibilities for future work are outlined below:

- Amorphous carbon multilayers with graded interfaces prepared by periodic bias could be annealed at high temperatures and their structure and stress investigated. This would allow further investigation of the role of stress in determining microstructure.

- Molecular dynamic simulations which take into account the effect of energetic ions may provide relevant information in regards to the graded interface of a-C/a-C multilayers with a cathodic arc deposition.

- Continued investigation into producing optimal nanostructure multilayer systems by modifying the deposition conditions. Depositing a complete set of Al/a-C multilayers for a range of period thicknesses would be interesting.

- An investigation into plasma transport properties during magnetron sputtering and cathodic arc deposition including the effect of charge states, incident ion energy, magnetic field strength etc. on film formation and growth mechanisms. Understanding the deposition systems and growth modes more clearly would improve the likelihood of creating superior coatings.

- Further microscopy to improve the degree of characterization performed. The use of a Field Emission TEM (FEGTEM) and a Focus Ion Beam (FIB) to allow HRTEM to be performed at the specific locations of indents following hardness measurements. The TEM and EELS performed in this thesis was performed on an instrument with a thermionic gun which limited the resolution. Access to a FEGTEM would allow clearer identifications of the microstructure of nano-structured coatings and the
mechanism associated with any enhancement in mechanical properties.