



# Studies on the influence of sputtering power on amorphous carbon films deposited by pulsed unbalanced magnetron sputtering



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## ABSTRACT

Amorphous carbon (a-C) films were deposited by pulsed unbalanced magnetron sputtering technique under different sputtering powers from 100 to 220 W. The film thickness, bonding configuration, mechanical and optical properties of these films were investigated by various techniques. It is found that the film thickness of a-C films increases with the increase of sputtering power. The results of X-ray photoelectron spectroscopy analysis suggest that the  $sp^3/sp^2$  ratio in the films increases with increasing sputtering power from 100 to 180 W, and then decreases with increasing sputtering power from 180 to 220 W. Mechanical and optical properties measurements show that the nanohardness, refractive index and optical band gap increase with increasing sputtering power from 100 to 180 W, and then decreases with the further increase of sputtering power; the extinct coefficient decreases first and then increases with increasing sputtering power. The results above indicate that sputtering power has a significant influence on the microstructure and properties of a-C films deposited by pulsed unbalanced magnetron sputtering technique.

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## 1. Introduction

In recent years, amorphous carbon (a-C) films have attracted considerable attention because of their particular properties such as high hardness, low friction coefficient, good wear-resistance, transparency over wide wavelength region, a wide optical band gap, high electrical resistivity, high chemical inertness, and outstanding biocompatibility [1–3]. Therefore, a-C films have been used in a wide range of industrial applications such as anti-reflection protective coatings for IR windows and solar cells, protective coatings for magnetic disks and tool materials, micro-electronic and photonic devices, and biomedical coatings [1–3]. It is well known that a-C films are metastable and in amorphous phase of carbon consisting of a mixture of  $sp^3$  (diamond-like) and  $sp^2$  (graphite-like) bonding structures. A large number of previous studies have shown that the characteristics and properties of a-C films were strongly depended on the  $sp^3/sp^2$  ratio, which is predominantly controlled by the preparation methods and the deposition parameters [3–6]. As a result, the electrical, optical,

conductive and mechanical properties can be tailored over wide range [3–6]. a-C films therefore have been prepared by various relevant methods, such as plasma enhanced chemical vapor deposition, magnetron sputtering, cathodic vacuum arc deposition, ion beam deposition, pulse laser deposition and plasma based ion implantation [1–7]. Among these methods, pulsed unbalanced magnetron sputtering is found to be one of the most suitable and widely used techniques to formulate a-C films. This technique has several advantages [1,7,8]: (1) the unbalanced magnetic lines of force can be adjusted to improve ionization effects from target species and maintain a non-equilibrium plasma state for sputtering on the substrate; (2) it can cause ions effective bombarding on the growing film leading to improvement of the adhesion of the films to substrate and modification of the properties of the films; (3) it can steadily increase the deposition rate; (4) it can significantly reduce the formation of arcs during film preparation, and hence, can reduce the number of defects and improve the quality of the deposited films. As the pulsed unbalanced magnetron sputtering process is more complex than the conventional magnetron sputtering, so the microstructure and properties of the a-C films deposited by this method are valuable to be investigated in depth.

For a pulsed unbalanced magnetron sputtering deposition system, sputtering power is one of the most important deposition

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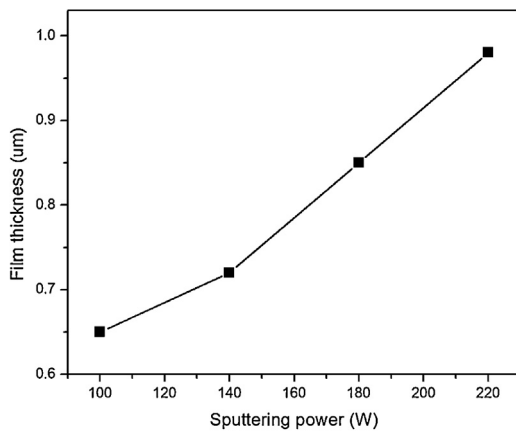


Fig. 1. Film thickness of a-C films as a function of sputtering power.

parameters which influence the energy of carbonaceous species sputtered from the target. To explore the suitable deposition conditions for a-C films with high-quality, it is interesting to study the sputtering power dependence in the case of pulsed unbalanced magnetron sputtering technique. In this study, a-C films were prepared by pulsed unbalanced magnetron sputtering technique under different sputtering powers, and the microstructure, mechanical and optical properties of the deposited films were investigated.

## 2. Experimental

Amorphous carbon (a-C) films were deposited on the mirror polished Si (100) wafers by pulsed unbalanced magnetron sputtering technique using Ar (purity 99.99%) as sputtering gas. Before being transferred into the vacuum chamber, the substrates were ultrasonically cleaned in acetone and ethanol for about 10 min, and then rinsed in deionized water, and finally dried. A base pressure about  $3 \times 10^{-4}$  Pa was attained in the chamber with a turbomolecular pumping system. The surface of the substrate was bombarded by Ar plasma at 2 Pa with 700 V bias voltage for more than 15 min to remove the surface contaminations and to activate the surface prior to film deposition. The pressure in the chamber was changed to 0.26 Pa, due to adding Ar gas into the discharge chamber during film deposition. A graphite plate (99.99% purity) was used as sputtered target. The distance between substrate and target is 90 mm. The bias on the substrate was fixed at 100 V pulsed at 40 kHz (80% duty cycle). The deposition time of the samples was 2 h. A pulsed electrical source with 80% duty cycle at 40 kHz was used. And a group of samples was prepared at different sputtering powers in the range of 100–220 W at room temperature.

The film thickness was measured by surface profilometer (TenCor Alpha-Step IQ). A RM2000 instrument from Renishaw, U.K. with a 514.5 nm Ar<sup>+</sup> laser source was used for Raman spectra analysis. X-ray photoelectron spectroscopy (XPS) studies were carried out on the deposited films using a PHI Quantera SXM system with monochromatic Al K $\alpha$  radiation (1486.6 eV). The refraction index and extinct coefficient of the films were determined by a M-2000DI spectroscopic ellipsometer (SE) at the wavelength of 1600 nm. The optical band gap was estimated by the transmittance spectrum, which was measured with UV–visible spectrometer (Perkin Elmer Lambda12).

## 3. Results and discussion

Fig. 1 shows the film thickness of the amorphous carbon (a-C) films deposited at different sputtering power. It can be observed

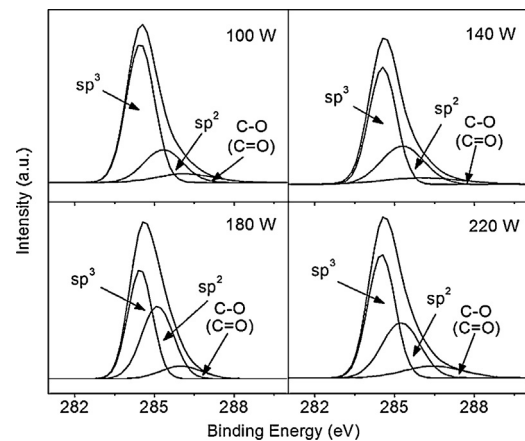


Fig. 2. Deconvoluted XPS C1s spectra of the a-C films deposited at different sputtering powers.

that the film thickness of a-C films increased with the increase of sputtering power. This result clearly shows that sputtering power has an obvious effect on the a-C film thickness. High sputtering power increases the degree of gas dissociation resulting in the production of more Ar<sup>+</sup>, which strikes the target with higher energy [9]. And the sputtering yield of the graphite target increases with increasing sputtering power. Therefore, the film thickness of a-C films increased with increasing sputtering power.

XPS is a powerful surface sensitive technique in which the core level chemical shifts are measured which are valuable for understanding the local environment of an atom, for example, in investigating whether a carbon film is sp<sup>3</sup> or sp<sup>2</sup> bonded. Apart from the chemical shift, the XPS technique can provide other useful information such as film composition, plasmon energy, valence band density of states, etc [10]. In order to determine the bonding states in detail and obtain the sp<sup>3</sup> content in the a-C films, XPS analysis was employed. Fig. 2 shows the deconvoluted XPS C1s spectra of a-C films deposited at different sputtering powers. And the binding energies, full width at half maximum (FWHM) values and the areas under the peaks are then obtained via the Gaussian fitting method. It is usually assumed that a-C film consists of carbon atoms of both sp<sup>3</sup> and sp<sup>2</sup> configurations, thus its corresponding C1s peak may consist of two groups of C1s photoelectrons, one from the carbon atoms in the sp<sup>3</sup> configuration and the other from the carbon atoms in the sp<sup>2</sup> configuration. Changes in the line shape, peak position and FWHM of the XPS C1s spectra can be observed as the sputtering power is increased, indicating the transformation between sp<sup>3</sup> sites and sp<sup>2</sup> sites with the increase of sputtering power. As shown in Fig. 2, all C1s XPS spectra of the a-C films consist of three sub-peaks that correspond to the different chemical binding states. The first peak located at about 284.5 eV is attributed to sp<sup>2</sup> hybridized carbon atoms, while the second peak located at about 284.5 eV is attributed to sp<sup>3</sup> hybridized carbon atoms [1,7,11]. The third peak in the binding energy ranging from 286 to 289 eV is due to some carbon atoms are bonded to oxygen (C–O or C=O) on the film surface [1,7,11]. The sp<sup>3</sup>/sp<sup>2</sup> ratio can be estimated from the area ratio of the sp<sup>3</sup> to sp<sup>2</sup> peak [1,7,11]. Fig. 3 shows the sp<sup>3</sup>/sp<sup>2</sup> ratio in the a-C films calculated from XPS as a function of sputtering power. It can be seen that the sp<sup>3</sup>/sp<sup>2</sup> ratio in the films increases with increasing sputtering power from 100 to 180 W, while decreases with increasing sputtering power from 180 to 220 W. The variation trends of sp<sup>3</sup> content in the present films can be well explained by the sub-plantation model [1,7,12]. According to sub-plantation model, the conversion of sp<sup>2</sup> to sp<sup>3</sup> carbon in a-C films can be controlled by adjusting the impinging carbonaceous species energy. When the energy of an impinging species is less than the energy of

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