

Investigating the structural and physical properties of hydrogenated amorphous carbon films fabricated by middle frequency pulsed unbalanced magnetron sputtering



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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) films were deposited by the middle frequency pulsed magnetron sputtering method using a graphite target in a mixed methane and argon plasma. The effects of substrate bias on the microstructure, surface morphology, mechanical, electrical and optical properties of the a-C:H films were investigated. It has been found that the sp^3 fraction in the a-C:H films increases with increasing substrate bias from 0 to 150 V. AFM measurements show that the RMS surface roughness of the films decreases with increasing substrate bias from 0 to 150 V. The correlation between the sp^3 fraction and surface roughness of the a-C:H films is revealed, and the mechanism on it is suggested in this paper. Nanoindentation, electrical and optical measurements indicate that the nanohardness, electrical resistivity and optical band gap increase with increasing substrate bias from 0 to 150 V. The results above are useful for the practical application of a-C:H films.

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1. Introduction

Hydrogenated amorphous carbon (a-C:H) films have attracted considerable attention due to their unique properties such as high hardness, low-friction coefficient, good wear-resistance, high optical transparency, high electrical resistivity, chemical inertness and biocompatibility [1–4]. These properties result in its wide-spread applications as protective coatings in areas such as optical windows, magnetic storage disks, tapes, automotive components, biomedical coatings and micro-electromechanical devices [1,3,4].

Many methods are used to synthesize a-C:H films including plasma enhanced chemical vapor deposition, cathodic vacuum arc deposition, pulse laser deposition, ion beam deposition, plasma based ion implantation and magnetron sputtering [4,5]. Magnetron sputtering is one of the most common processes to formulate a-C:H films, owing to its good reproducibility, good controllability, high deposition rate and low processing temperature. However, in the conventional sputtering methods, plasma density is relatively low so that the ionization effect is small, affecting the quality of a-C:H films [5]. The unbalanced magnetron sputtering (UBMS) has several advantages: (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 [4–7]. And such a method with pulsing the targets in the medium frequency range can significantly reduce the formation of arcs during film preparation, hence, can reduce the number of defects and improve the quality of the deposited films [4,7]. As the middle frequency pulsed unbalanced magnetron sputtering (MFPUMS) process is more complex than the conventional magnetron sputtering, so the microstructure and properties of the a-C:H films deposited by this method are valuable to be investigated in depth.

Previous studies have shown that the microstructure, composition and properties of a-C:H films were strongly depended on the deposition methods and deposition parameters. Substrate bias is one of the most important parameters which should affect the energy of carbonaceous species reached the substrate and the properties of a-C:H films. The influence of substrate bias on the a-C:H deposited by magnetron sputtering has been reported. However, the results are not always simple. For example, Ahmad et al. [8] reported that the electrical resistivity of the a-C:H films deposited by UBMS increases when the substrate bias increases from 0 to 100 V, then decreases from 100 to 300 V. On the other hand, Park et al. [9] reported that the electrical resistivity of the a-C:H films deposited by UBMS decreases with substrate bias voltage from 0 to 200 V. This suggests that the effect of the substrate bias on the properties may depend on the sputtering system. To explore the suitable deposition conditions for a-C:H films with high-quality, it is interesting to investigate the substrate bias dependence in the case of MFPUMST. In this study, a-C:H films were prepared by MFPUMST and the effects of substrate bias on

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the structure, surface morphology, mechanical, electrical and optical properties of the a-C:H films were investigated.

2. Experimental

a-C:H films were deposited on the mirror polished Si (100) and glass wafers by middle frequency pulsed unbalanced magnetron sputtering (MFPUMST) using CH₄ (purity 99.99%) and Ar (purity 99.99%) as the carbon source gas and sputtering gas of graphite targets (100 mm in diameter and 3 mm in thickness). 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 5×10^{-4} Pa was attained in the chamber with a turbomolecular pumping system, and 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 3×10^{-1} Pa, due to putting Ar gas and then CH₄ gas into the discharge chamber during film deposition. The distance between substrate and target is 90 mm. The target current was set at 300 mA pulsed at 40 kHz (80% duty cycle). A pulsed bias electrical source with 80% duty cycle at 40 kHz was used. A group of samples was prepared at different pulsed negative bias voltages from 0 to 150 V at room temperature with a CH₄/(CH₄+Ar) ratio of 50%. The deposition time of the samples was 4 h.

A RM2000 instrument from Renishaw, U.K. with a 514.5 nm Ar⁺ 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 α radiation (1486.6 eV). The surface morphology was examined by a SPA-400 atomic force microscope (AFM), the root mean square (RMS) surface roughness was measured using the same technique. The mechanical properties of a-C:H films were measured by a fully calibrated Nano Indenter XPTM of MTS Systems Corporation, a triangular pyramid tip of Berkovich diamond was used. The electrical resistivity of a-C:H films was measured using a four-point probe equipment at room temperature. The optical band gap was estimated by the transmittance spectrum, which was measured with UV-visible spectrometer (Perkin-Elmer Lambda12).

3. Results and discussion

The chemical composition, oxidation states and structural properties of the a-C:H films were studied quantitatively by XPS. The C1s XPS spectra of the films deposited under different substrate bias are shown in Fig. 1, and the fitting of XPS C 1s core level spectra was performed by peak fit software using the Gaussian component. As amorphous carbon film consists of both sp³ and sp² configurations of carbon, the C1s XPS spectra are mainly composed of two groups of C1s photoelectrons, one from carbon atoms in the sp³ configuration and the other from the sp² configuration. As shown in Fig. 1, all C1s XPS spectra of the films consist of three sub-peaks that correspond to the different chemical binding states. The peaks centered at approximately 284.6 eV and 285.5 eV represent the sp² and sp³ carbon bonding, respectively. The third peak located at about 286.2 eV is attributed to C–O contamination formed at the surface of the samples due to air exposure [10–14].

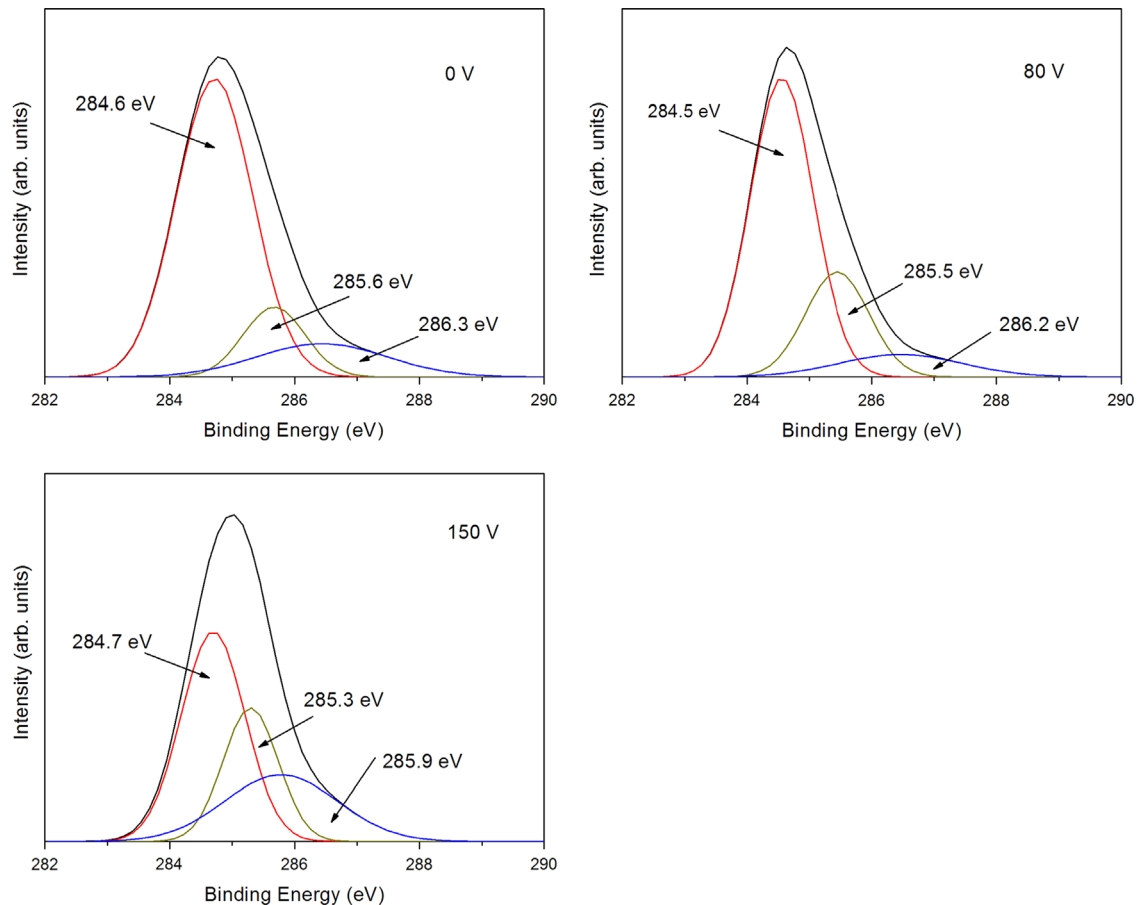


Fig. 1. XPS spectra of a-C:H films deposited under different substrate bias.

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