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Structural, optical and electrical properties of 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 method, the effects of substrate temperature on the structure, optical and electrical properties of the a-C films were investigated. It has been found that the sp^3 fraction in the a-C films increases with increasing substrate temperature from 50 to 100 °C, while decreases with increasing substrate temperature from 100 to 200 °C. Optical and electrical measurements show that the refractive index, optical band gap and electrical resistivity are strongly dependent on the substrate temperature. The a-C films deposited at 100 °C have higher refractive index, optical band gap and electrical resistivity. The possible reason for all the above observation was discussed. The results above are useful for the practical application of a-C films.

1. Introduction

The amorphous carbon (a-C) films exhibit a lot of excellent properties such as tunable optical properties, infrared transparency, high hardness, excellent wear resistance, low friction coefficient, high electrical resistance and chemical inertness, which make it feasible for them to be widely used in optics, mechanical engineering and materials science [1–4].

a-C films could be synthesized by various techniques such as plasma chemical vapor deposition, filtered cathodic arc technique, pulsed laser deposition and sputtering [1–4]. Magnetron sputtering is one of the most common processes to formulate a-C films. However, in the conventional sputtering methods, plasma density is relatively low so that the ionization effect is small, affecting the quality of a-C films [5]. The magnetron sputtering technique in pulsed unbalanced mode has several advantages. Firstly, 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. Secondly, 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. Thirdly, it can steadily increase the deposition rate. Fourthly, it can significantly reduce the formation of arcs during film preparation due to pulsing the magnetron discharge, hence, reduce the number of defects and improve the quality of the deposited films [5–7]. 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.

A large number of previous research results have indicated that the structure and properties of the amorphous carbon films are strongly depend on deposition process parameters, for instance, substrate temperature, substrate bias, deposition pressure, and so on [1,3–7]. During these factors, substrate temperature is a fairly critical deposition parameter that influences the mobility of the depositing particles at the substrate. In this paper, the effects of substrate temperature on the structural, optical and electrical properties of the a-C films deposited by pulsed unbalanced magnetron sputtering were investigated.

2. Experimental

Amorphous carbon films were deposited on the mirror polished Si (1 0 0) and glass wafers by pulsed unbalanced magnetron sputtering technique. 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

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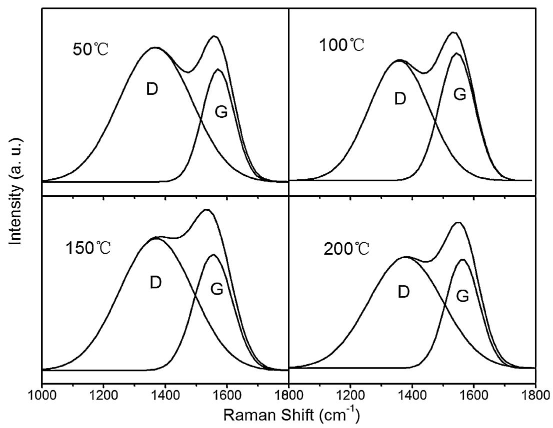

Fig. 1. Raman spectra of the a-C films deposited at different substrate temperatures.

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 putting Ar gas into the discharge chamber during film deposition. The purity of Ar was 99.99%, and a graphite plate (99.99% purity) with a size of 100 mm in diameter and 3 mm in thickness was used as sputtered target. The distance between substrate and target was 90 mm. The power input to the target was fixed at 290 W by using a 40 kHz middle frequency electrical source with an 80% duty factor. The pulsed bias on the substrate was fixed at 100 V. A group of samples was prepared at different substrate temperature from 50 to 200 °C. The deposition time of the samples was 2 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 Kα radiation (1486.6 eV). The refraction index of the coatings was determined by a M-2000DI spectroscopic ellipsometer (SE) in the wavelength range from 1000 to 1700 nm. The optical band gap was estimated by the transmittance spectrum, which was measured with UV-visible spectrometer (Perkin Elmer Lamda12). The electrical resistivity of a-C films was measured using a four-point probe equipment at room temperature.

3. Results and discussion

Due to its availability and non-destructive nature, Raman spectroscopy is the most popular technique for characterizing amorphous carbon (a-C) structures and properties. Visible Raman spectra of a-C are dominated by scattering from the sp^2 sites. The spectra typically have two main peaks, the D peak around 1350 cm^{-1} and the G peak around 1560 cm^{-1}, which correspond to the breathing mode of the aromatic rings and the stretching mode of pairs of sp^2 sites in the aromatic rings or the olefinic chains [1,8]. The parameters of Raman spectra such as positions, full-width-half maximum, and intensities of the D peak and G peak are closely related to the density, size, and structure of the sp^2 clusters [1,8]. These properties of sp^2 clusters are in turn closely related to the sp^3 content of a-C film, enabling us to measure the sp^3 content from the parameters of Raman spectra [1,7–9]. Fig. 1 shows the Raman spectrum of a-C films deposited under different substrate temperatures. Obvious difference between the spectra of the a-C films deposited at different substrate temperatures can be observed. The intensity ratio of the D peak and G peak (I_D/I_G) and the position of the G peak have been widely used for qualitative estimation of sp^3 content in a-C films, and a decrease of I_D/I_G and the shift of G peak position to lower wavenumber are indicative of the increase of sp^3 content in

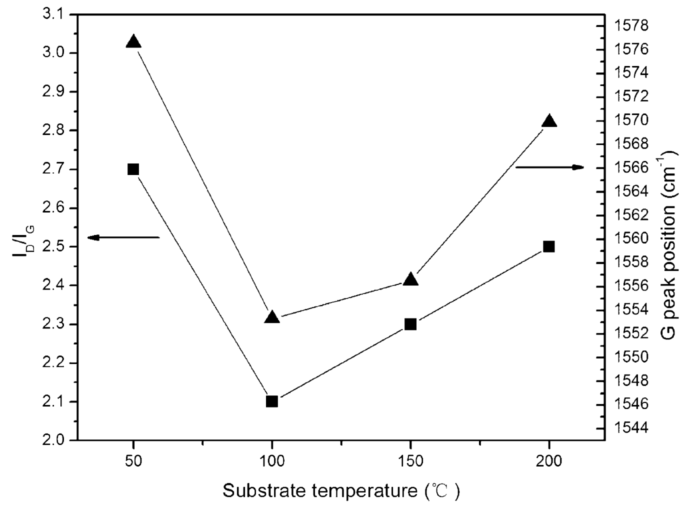

Fig. 2. The I_D/I_G ratio and G peak position of the a-C films as a function of substrate temperature.

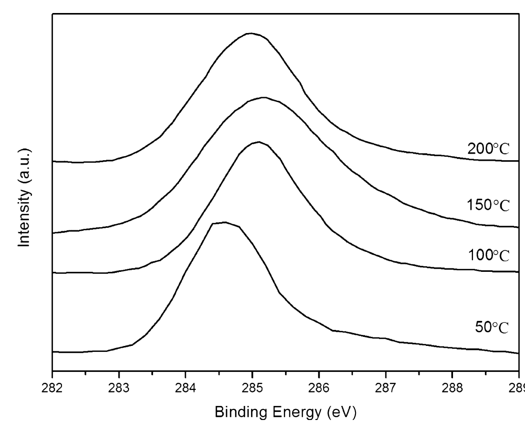

Fig. 3. XPS spectra of the a-C films deposited under different substrate temperatures.

a-C films [1,7,10]. The spectra were deconvoluted into two Gaussian lineshapes in order to obtain quantitative information about the sp^3 content in the films. Fig. 2 shows the I_D/I_G ratio and G peak position obtained from the Gaussian fitting results for these films. It can be observed that the positions of G peak moved to lower wavenumber and the I_D/I_G ratio decreased with increasing substrate temperature from 50 to 100 °C, and the positions of G peak moved to higher wavenumber and the I_D/I_G ratio increased with increasing substrate temperature from 100 to 200 °C. These variations generally indicate that sp^3 content increases with increasing substrate temperature from 50 to 100 °C, and then decreases with a further increase of substrate temperature. The results of Raman spectra measurements agree well with the data obtained by the XPS analysis, which is described below.

XPS spectroscopy is a powerful tool to determine chemical bonds of materials since each element has a unique set of binding energies. XPS was used to determine the detailed bonding structure of a-C films deposited under different substrate temperatures. The XPS C 1s spectra of the a-C films deposited under different substrate temperatures are shown in Fig. 3. Important changes in the line shape of the C 1s peak are detected as substrate temperature is increased. Generally speaking, the C 1s core peak can be deconvoluted into three Gaussian peaks around 284.7 eV, 285.2 eV and 286.5 eV, which are assigned to the C—C sp^2 bond, the C—C sp^3 bond, the C—O bond [11,12]. The C—O peak implies that the surface of the a-C films was slightly oxidized since the measurement