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Plasma treatment effects on hydrogenated amorphous carbon films prepared by plasma-enhanced chemical vapor deposition

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Abstract

When hydrogenated amorphous carbon (a-C:H) films are deposited by a radio frequency (RF; 13.56 MHz) glow discharge system, their properties can be significantly affected by RF power input at deposition. Furthermore, the hydrogen content in the a-C:H films will be decreased in the postdeposition plasma treatment. This study investigated the effects of plasma input at deposition and postdeposition plasma treatment on the resulting film properties of a-C:H films. Atomic force microscopy (AFM) was employed to detect the surface roughness of the plasma-enhanced chemical vapor deposition (PECVD) a-C:H films. Raman spectroscopy was employed to determine the hydrogen concentration as well as the tetrahedral and trigonal bondings associated with C–H bond. The Raman analysis results suggested the occurrence of a higher degree of structural order in the sp^2 lattice of the well plasma-treated a-C:H films.
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1. Introduction

There has been a growing interest in hydrogenated amorphous carbon (a-C:H) thin films due to their unique properties, such as high hardness and dielectric strength, chemical inertness to both acids and alkaline, transparency for infrared light, and a low coefficient of friction [1]. Hydrogenated amorphous carbon (a-C:H) thin films are applied as protective coating on magnetic recording disks, optical devices, etc. The properties of these alloys are determined by the hybridization of carbon atoms, by the relative concentrations of different bonds, and by the distribution of hydrogen among different types of carbon atoms. Being deposited by radio frequency (RF) plasma from hydrocarbons, the film properties are strongly influenced by the energy of the film forming particles. The energy is, in turn, determined by the deposition parameters. In order to obtain the desired physical properties during deposition, it is important to understand the relationship between the observed physical properties, the chemical structure, and their correlation with the preparation conditions.

There exist different kinds of carbon bonds in these films: sp^3, sp^2, and sp^1 as well as various C–H bonding configurations [2]. The properties of these films are closely related to the sp^2/sp^3 ratio, the H content, and the degree of short-range order in the structure. In this paper, we will describe the effects of plasma ion energy on the surface roughness and chemical bonding ratio of a-C:H thin films. Atomic force microscopy (AFM) was employed to detect the surface roughness of the plasma-enhanced chemical vapor deposition (PECVD) a-C:H films. The sp^2/sp^3 ratio in the bulk of the films was characterized by Raman spectroscopy. The effect of postplasma treatment on the a-C:H films was also investigated from the evolution of Raman spectra.

2. Experimental

The experiments were performed on a number of amorphous hydrogenated carbon films prepared by PECVD. The a-C:H films were deposited on silicon

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substrates in a 13.56 MHz RF ethane glow discharge system. The pressure was kept at 6 Torr, while the plasma power was varied from 0.8 to 2.4 kW. The substrate temperature during deposition was kept at 400°, while the postplasma treatment was conducted in situ after the deposition process, with argon ions at RF power of 1.8 kW and 6.0 Torr of chamber pressure. The surface topographies were examined using AFM (DINanoScope III), with the scan size of each AFM image being 10 μm × 10 μm. The mean surface roughness (R_a) of the films was obtained from AFM scan. The Raman spectra was obtained in the backscattering configuration, and collected using a spectrometer coupled with an optical microscope. The measurement was performed in the 1000–2000 cm^{-1} region by using a single-stage spectrometer (Action SprectraPro 500I). Each sample was illuminated with an ion argon laser of wavelength 514.5 nm, focused to a ~50 μm round spot. A longitudinal optical peak at 1590 cm^{-1} is the characteristic of crystalline graphite and is called the G peak. The shoulder peak at around 1380 cm^{-1} caused by disorder is called the D peak. These two spectral features will provide information on sp^2 clustering in the amorphous matrix. The film thickness and refractive index were determined by a spectroscopic ellipsometer at a 74.9° incident angle and 633 nm wavelength.

3. Results and discussions

The ion energy at the deposition of PECVD a-C:H films will modify both surface topography and film structure. The modification can be ascribed to numerous phenomena, such as sputtering, implantation, diffusion,

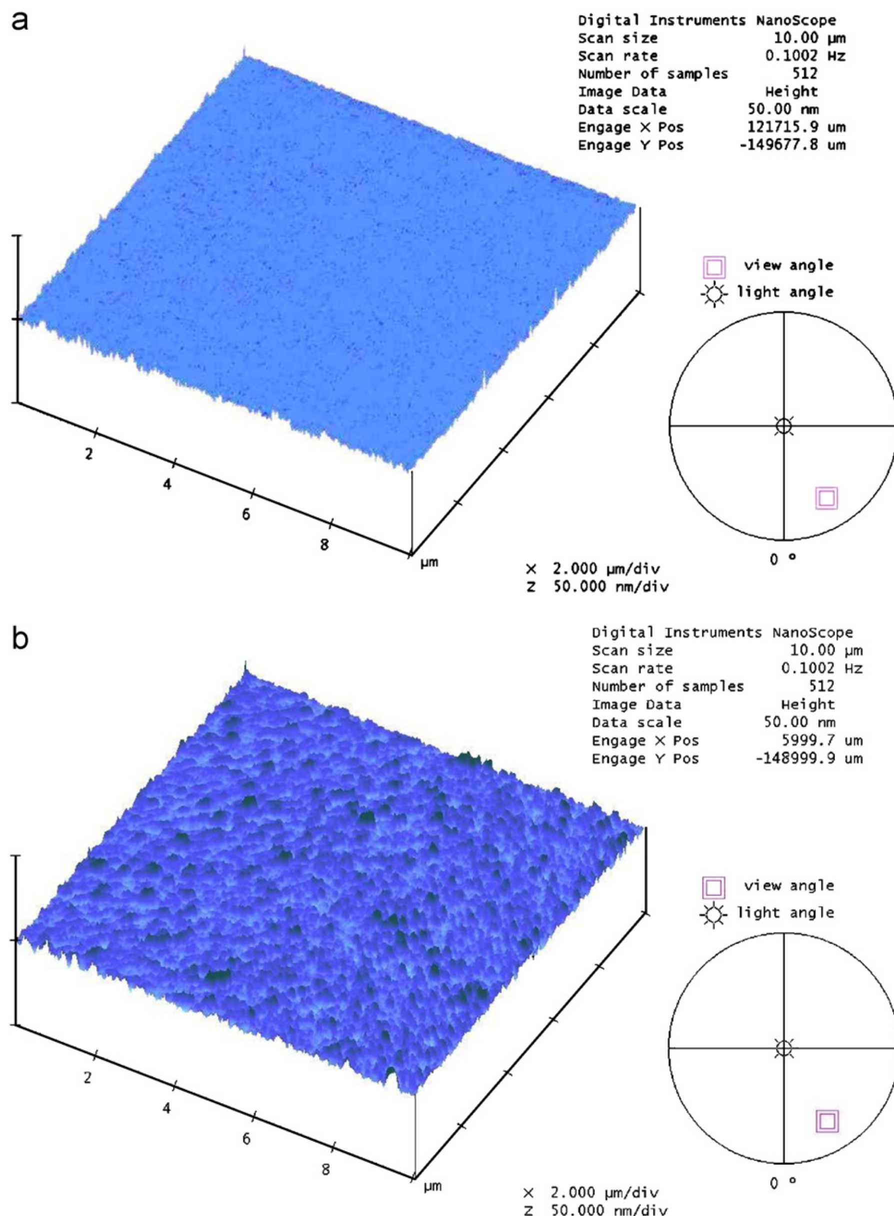

Fig. 1. Three-dimensional AFM images of PECVD a-C:H films deposited at (a) 0.8 kW and (b) 2.4 kW of RF plasma. The scanning size is 10 μm × 10 μm.

and redeposition effects [3]. AFM measurements have been performed to investigate a more detailed surface topography. Fig. 1 shows the AFM analysis of surface roughness for a-C:H films deposited at 0.8 and 2.4 kW. AFM result indicates that the surface roughness of the a-C:H films increases with the RF plasma power input during film deposition. Significant roughening of the surface is observed for a-C:H films deposited at 2.4 kW. Fig. 2 illustrates the correlation of mean surface roughness (R_a) and the RF power energy at deposition for PECVD a-C:H films. A gradual increase in the roughness of film surface was observed at RF power between 0.8 and 1.8 kW. Nevertheless, as the RF power at deposition of PECVD a-C:H film is above 1.8 kW, the surface roughness increases at a higher ramp rate. At relatively low ion energy, the surface topography is reconstructed. This gradual increase of surface roughness indicates persistent destruction of chemical bonds, which develops internal surfaces in the clustered carbon network. At too high the RF plasma, when very energetic carbon ions were used, the strong sputtering effects can lead to effective destruction of the carbon network during its formation, and, consequently, mounding roughening at the surface was observed [4,5].

For the a-C:H, both the film and the impinging ions are rich in hydrogen. During subsurface accommodation, hydrogen impedes formation of new C–C bonds and so limits the amount of carbon–carbon bonding. Increasing the RF power can break the C–H bonding more easily thus resulting in the decrease in the hydrogen content and a transition from tetrahedral bonding to trigonal bonding. Fig. 3 demonstrated the Raman intensity of PECVD a-C:H films deposited at various RF plasma power. With increasing RF power, the Raman spectra evolve continuously to higher peak intensities, and thus result in a gradual shift of the G line peak position to lower wave numbers. The changes in the shape of the spectra along with the relative peak intensities, reflect the structural changes in the films, which are mainly due to an increasing sp^2 and therefore also the decrease of hydrogen concentration with increasing ion energy [6]. The observed shift of the G line can be ascribed to the modification of disorder and the clusterization of a mainly sp^2-bonded carbon network with a high concentration of implanted carbon atoms [7]. Though it was reported elsewhere that ion inhibits the graphitization either directly, through the destruction of the graphitic cluster, or indirectly, through a densification of the matrix structure [8], the decrease of I_d/I_g peak intensity ratio with increasing RF plasma for a-C:H films still indicates that the degree of graphitization for the a-C:H films depends strongly on the ion energy chosen for the film deposition.

Fig. 4 compares the Raman spectra in the vicinity of the D peak (wave number~1380 cm^{-1}) of PECVD a-C:H film as-deposited and subjected to in-situ postplasma treatment.

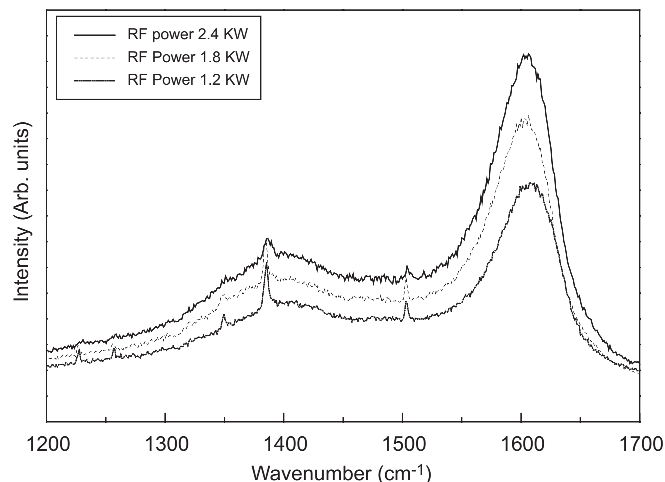

Fig. 3. Raman spectra of PECVD a-C:H films deposited at (a) 1.2 kW, (b) 1.8 kW, and (c) 2.4 kW of RF plasma power.

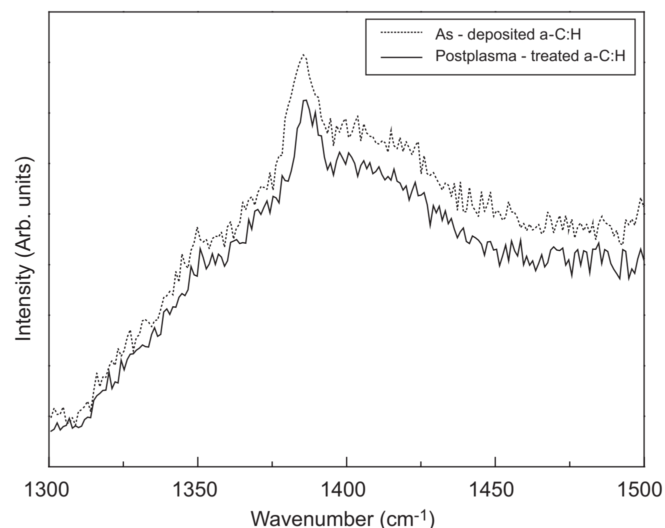

Fig. 4. Raman spectra of PECVD a-C:H films (a) as-deposited and (b) 1.8 kW postplasma-treated.

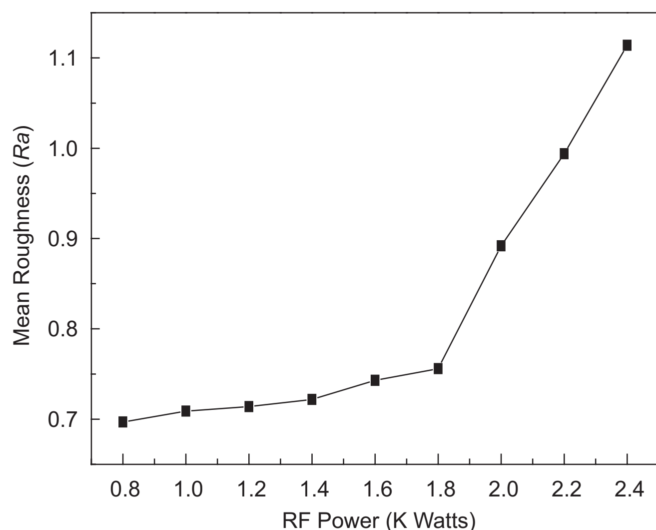

Fig. 2. Variation of the mean surface roughness of PECVD a-C:H films with the RF plasma.

Raman spectra showed that the postplasma treatment results in the decrease of the D-line peak intensity, indicating an increase of sp^2 coordination thereby generating more ordered graphite. Since hydrogen atoms will preferentially be bonded to C (sp^3) atoms in a-C:H films [9], the increase of sp^2 carbon fraction also implicates the loss of hydrogen. In the postplasma treatment of a-C:H films, the energetic particles persistently destroy the loosely bounded C–H chemical bonds, thus allowing a more stable C–C bonding to be formulated. The observed evolution of the Raman spectra of the postplasma-treated a-C:H films suggests the thermodynamic instability of the as-deposited PECVD a-C:H films. In the case of postplasma-treated a-C:H films, the amount of unbounded and loosely bounded molecules in the structure can be reduced significantly, and a structure relaxation process can proceed to a thermodynamic minimum of energy.

4. Conclusions

In this study, the effects of plasma ion energy on the surface roughness and chemical bonding ratio were investigated. The surface roughness increases with increasing RF plasma power. The increase of RF plasma power also leads to the increase of sp^2 bonding and the decrease of hydrogen concentration in PECVD a-C:H films. The postplasma treatment destroys the loosely bounded C–H chemical bonds, thus reducing the hydrogen content, and helps develop a more stable C–C bonding.

Acknowledgments

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