Influence of deposition temperature on the structure, optical and electrical properties of a-C films by DCMS

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ABSTRACT

Amorphous carbon films have been considered as strongly promising semiconductor materials, due to their superior mechanical properties, specific bond structures, as well as facile deposition over large area with device integrated processes. To figure out the effect of sp2/sp3 ratio and size of sp2 clusters on opto-electrical behavior, we fabricated a series of H-free amorphous carbon (a-C) films by magnetron sputtering with a controllable deposition temperature from 30 to 400 °C. Results showed that all the films displayed a strong light absorption in the ultraviolet and visible regions, where the transmittance was less than 5% in the wavelength range of 200–750 nm, demonstrating the typical semiconductor behavior in temperature from 5 to 350 K, exhibiting a lower resistivity at higher temperature. In addition, their transmittance, optical bandgap, resistivity and activation energy showed similar tendency with increasing deposition temperature, which was discussed in terms of the evolution of sp2/sp3 ratio and sp2 cluster in the a-C films. These studies provide a new route to tune optical and electrical properties of a-C films for their opto-electrical applications.

1. Introduction

Amorphous carbon (a-C) films with specific atomic bond structures have been widely used in various areas as protective and multifunctional materials on account of their outstanding mechanical and tribological properties, such as high hardness, low coefficient of friction and good chemical inactivity [1–5]. Furthermore, as amorphous semiconductor materials, their resistivity can span in a wide range from 102 to 1016 ohm·cm [6], the optical band gap can also be adjusted at 0.8–4.0 eV, which is strongly dependent on the deposition conditions. Very recently, a-C films have shown great potential in the field of optoelectronic devices, such as piezoresistive sensors, field emission cathodes, infrared detecting and optical windows [7–10].

To meet the highly demanded opto-electrical applications, however, it is still an opening challenge to figure out the main factors affecting opto-electrical properties of a-C films. For example, Dai and co-workers reported that both the sp3 and sp2 hybrid bonds dominated the opto-electrical properties of a-C films, since the optical bandgap and electrical resistivity were positively correlated with the ratio of sp2/sp3 bonds [11]. Besides, Mohagheghpour et al. pointed out that the electrical properties of a-C films showed the strong dependence on the size and distribution of sp2 clusters [12]. Meanwhile, Caro et al. presented a computational study of tetrahedral amorphous carbon surfaces within density functional theory [13–15]. They considered the degree of localization of the electronic states was obtained with a participation ratio analysis, showing a direct relation with density and sp2 fraction. In addition, Sze and co-workers demonstrated that the optical bandgap of a-C films deposited by plasma immersion ion implantation (PIII) decreased with increasing substrate bias voltage, due to the graphitizing of the a-C films [16]. Furthermore, Guo et al. observed the carrier transport of a-C was dominated by the thermally activated process with an activation energy of 0.1576 eV in the temperature range of 160–400 K [7,17]. Based on the previous studies, at least three factors will determine the opto-electrical properties of a-C films, namely, sp2/sp3 ratio, size and distribution of sp2 clusters. While, considering the complexity of atomic structures and variety of deposition methods, the relationship between composition, structure and opto-electrical properties of a-C films were still diverse, especially in consideration of...
designing high-performance carbon-based optoelectronic devices [18]. In this study, H-free a-C films were selected and prepared by direct current magnetron sputter (DCMS) technique. The composition and structure of a-C films were adjusted by changing deposition temperature from 30 to 400 °C. The dependence of sp²/sp³ ratio and sp² clusters on the opto-electrical properties of a-C films was systematically studied.

2. Experimental details

The a-C films were deposited by DCMS (P600-1) with a supplied graphite target (380 mm × 100 mm × 7 mm) of 99.99% purity, as shown in Fig. 1 [19]. The P type Si (1 0 0) wafer, quartz and Al₂O₃ (0 0 0 1) were used as substrates. The substrates were cleaned step by step in ultrasonic bath of acetone and alcohol, respectively, before loaded into the deposition chamber. When the chamber vacuum (background vacuum) reached 3 × 10⁻³ Pa, all the substrates were cleaned by Ar⁺ glow discharge at a bias of −350 V for 30 min. During deposition, the power of DC magnetron sputtering was kept at 1.7 kW, that was the power density was about 4.47 W/cm², with negative DC bias −300 V. The thicknesses of all the a-C films were maintained at around 190 ± 30 nm by changing the deposition time.

The thickness and deposition rate of a-C films prepared at various temperature are listed in Table 1. As the deposition temperature increased from 30 °C to 400 °C, the thickness of a-C films increased from 162 nm to 219 nm, with the corresponding deposition rate increasing in order to remove surface contamination. Here, the sp² contents in the a-C films were determined from the C 1s XPS spectra, with a mixture of a Gaussian (20%) and a Lorentzian (80%) function used to fit the sp²-C peak and sp³-C peak after a Shirley background subtraction [20–22]. The atomic bonding structure of the films was characterized by a Raman spectroscopy (Renishaw in Via-reflex, 532 nm) at a detecting range from 800 to 2000 cm⁻¹. The microstructure of the a-C film deposited at room temperature was examined by high-resolution transmission electron microscopy (TEM, Tecnai F20, US) with operating voltage 200 kV, and the sample for TEM observation was prepared with Focused Ion Beam (FIB) instrument (Carl Zeiss, Auriga).

The transmittance of the deposited a-C films was tested by Fourier transformation infrared spectrum (FTIR, Thermo, US) in the wavelength range from 2.5 to 15 μm, with a resolution of 1 cm⁻¹ and scanning wavenumber range from 400 to 2000 cm⁻¹, and ultraviolet–visible spectrophotometer (Lambda 950, US) in the wavelength range from 15 to 25 μm, with scanning step size 1 nm. And the samples for transmittance test were deposited on quartz substrates [23,24]. The room temperature resistivity, current-voltage (I-V) feature of the samples was measured by Hall-effect measurement (Nanometrics, HP-5500C, US). The temperature dependence of dark electrical resistivity (ρ) of the a-C films was tested by physical property measurement system (PPMS, Quantum Design, Model-9) in a standard 4-probe way along with the temperature range of 5–350 K.

3. Result and discussion

3.1. Thickness and morphology

The thickness and deposition rate of a-C films prepared at various temperature are listed in Table 1. As the deposition temperature increased from 30 °C to 400 °C, the thickness of a-C films increased from 162 nm to 219 nm, with the corresponding deposition rate increasing
Raman spectra were shown in Fig. 4(a). In order to obtain the bond arrangements, furthermore, the sp² and sp³ contents could be deduced as shown in Fig. 3(b). With increasing deposition temperature when the deposition temperature was below 400 °C, the sp² content increased mildly from 5.4 nm/min to 7.3 nm/min, because the surface bonding force between carbon particles and the substrate increased with increasing deposition temperature when the deposition temperature was below 400 °C [25–29].

The tapping mode 2D-AFM images and the corresponding 3D-AFM images of the films at different temperature are shown in Fig. 2. Overall, all the a-C films showed continuous, uniform and smooth surfaces, despite the surfaces became rough slightly with elevated temperature, where the Rq increased from 0.4 nm at 30 °C to 6.0 nm at 400 °C, as illustrated in Table 1. The evolution of the surface morphology could be explained from the diffusion process during deposition of a-C films, in which the carbon atoms adsorbed onto the surface attempted to gather into many clusters, resulting in a rougher surface at higher deposition temperature [28].

### 3.2. Chemical composition and structure

Fig. 3(a) demonstrates the influence of deposition temperature on the full XPS spectra at various deposition temperatures. All the a-C films were mainly composed of two elements C and O, the small amount of O element might come from the residual oxygen in the vacuum chamber during deposition and the oxygen absorbed by a-C film exposed in the air [29,30]. The XPS C 1s spectra (Inserts in Fig. 3(b)) were fitted into three dominant peaks approximately centered at 284.6 eV, 285.4 eV, 286.6 eV, corresponding to sp², sp³, and C–O=C=O hybridization, respectively [12,22,29,30]. By integrating the peak area, sp² and sp³ carbon hybridization ratio could be deduced as shown in Fig. 3(b). With increasing deposition temperature from 30 °C to 400 °C, the sp² content of a-C films increased from around 59% to 70%, implying that the C atoms in the films tended to form stable sp² phases at higher temperature and higher growth rates [12,21,31,32].

The Raman spectra of a-C films deposited at various temperatures on silicon substrates in the range from 800 to 2000 cm⁻¹ are shown in Fig. 4(a). In order to obtain the bond arrangements, furthermore, Raman spectra were fitted by two Gaussian peaks after a linear background subtraction [33–36]. Generally, G and D peaks are attributed to the vibration of sp² bonded carbon atoms [12], the G peak origins from the stretching vibration of sp² atoms in rings and chains, while D peak results from sp² atoms only in rings. The fitted G peak position, peak area ratio I_G/I_D and half maximum of G peak (FWHM) values, as shown in Fig. 4(b), can reflect carbon atoms disorder degrees, sp²/sp³ ratio, sp² cluster size and so on [37]. With the temperature changing from 30 °C to 400 °C, the G peak position shifted upward obviously from 1550 cm⁻¹ to 1578 cm⁻¹, which implied the increase of sp² contents [34,38,39] and coincided with the former XPS results. According to the cluster modes of amorphous carbon [34], all a-C films were in the transitional stage from amorphous carbon (G peak ~1510 cm⁻¹) to nanocrystalline graphite (nc-G) (G peak ~1600 cm⁻¹). In addition, the G FWHM decreased evidently from 171.5 to 134 cm⁻¹, indicating that the structure of a-C matrix became much more ordered; on the contrary, the I_D/I_G increased from its minimum value around 2.67 at 30 °C to its maximum value 4.25 at 400 °C. It could be inferred that the average size of sp² clusters decreased with increasing deposition temperature, since I_D/I_G varies inversely with the in-plane correlation length L in the transitional stage from amorphous carbon to nc-G [40].

In order to observe the microstructure of the a-C films directly, the typical cross-sectional TEM image, high resolution transmission electron microscopy (HRTEM) and the corresponding selected area electron diffraction (SAED) pattern of the typical a-C film deposited at 100 °C are displayed in Fig. 5(a) and (b). Apparently, the thickness of a-C film was around 200 nm and all the films exhibited a compact, uniform and fine cross-sectional morphology, and no nanocrystalline can be observed, as shown in Fig. 5(a). The corresponding SAED pattern just presented a weak diffuse halo, as shown in Fig. 5(b), which indicated that the sample had typical amorphous structure.

### 3.3. Optical properties

The transmittance of the films measured by FTIR were lower than 70% in the region of 2.5 to 25 μm, as depicted in Fig. 6(a), where the peak centered at 4 μm inferred samples owning dominant aromatic rings or olefinic chain and the peak centered at 15 μm is characteristic peak of CO₂ from atmosphere [2,41]. Different from monotonic structural evolution of a-C films with deposition temperature, the transmittance first decreased to its minimum value lower than 40% at 100 °C, then rose again with further increasing deposition temperature up to 400 °C. Similar phenomenon was also observed by UV–visible spectrophotometer from 0.2 to 1.5 μm, as shown in Fig. 6(b), and all the a-C films exhibited extremely low transmittance, lower than 5%, in the wavelength range of 200 to 750 nm which proved that these films had...
very strong light absorption properties in the range of ultraviolet and visible wavelength.

Tauc model is one of the most widespread used model to determine the optical properties of a-C films, and the band gap energy $E_{\text{opt}}$ can be calculated from $E(\varepsilon)^{1/2}$ as function of the incident energy $E$ [42]. The Tauc optical gap associated with the thin films is determined through an extrapolation of the linear trend observed in the spectral dependence of $(\alpha h\nu)^{1/2}$ over a limited range of photon energies $h\nu$. The Tauc optical gap is defined as occurring at the intercept of this linear extrapolation with the abscissa axis [43,44]. The absorption coefficient $\alpha$ near the band edge in a-C films shows an exponential dependence upon photon energy usually obeying the empirical relation,

$$\alpha = A(h\nu - E_{\text{opt}})^{n}/(h\nu)$$

where $A$ is the band edge parameter and $n$ is a number characterizing the transition process which may take values 1/2, 1, 3/2 or 2, depending upon the nature of the electronic transitions responsible for the absorption [45,46]. For a-C films, optical transitions are described to a first approximation by non-direct transitions with no conservation of electronic momentum, for allowed indirect transitions $n = 2$ [24]. Thus, the optical gaps for both indirect transitions could be determined by the extrapolation to zero of the linear regions in the plot of $(\alpha h\nu)^{1/2}$ vs. photon energy $h\nu$, as shown in Fig. 6(c).

I-V feature of a-C films was investigated by Hall-effect measurement, as shown in Fig. 7(a), all I-V plots exhibited a linear dependence, suggesting typical ohmic behavior. And the resistivity $R$ of the a-C films can be calculated from the I-V plots as displayed in Fig. 7(b), the $R$ first decreased from its maximum value $1.589 \times 10^{-2} \ \Omega \cdot \text{cm}$ at 30 °C to its minimum value $2.191 \times 10^{-3} \ \Omega \cdot \text{cm}$ at 100 °C, then increased monotonically with increasing deposition temperature to 400 °C.

Fig. 8 shows I-V plots of the films in the temperature range of 5 to 350 K, for the sample deposited at 30 °C, its I-V plots in the range of 5 to 50 K were not present here, since its resistance exceeded the upper limit of the instrument test range. Overall, all the samples displayed typical linear resistance characteristics in the range of 5–350 K, and their I-V plots were highly repeatable both during heating and cooling process, besides, the corresponding voltage of each sample decreased with increasing temperature at a certain excitation, which indicated the typical semiconductor behavior of the a-C films. In addition, at a certain test temperature, the sample deposited at 100 °C exhibited the lowest voltage compared with other samples at the same excitation, which matched well with the previous Hall-effect measurement.

In order to further explore its electrical properties, temperature dependence of dark resistivity (R-T) of the samples deposited at various temperatures was investigated, as shown in Fig. 9(a) and (b). In this test temperature range from 5 K to 350 K, the sample with a larger resistivity at room temperature also exhibited worse conductivity. Besides, the resistivity of all samples monotonically decreased with increasing temperature, and the sample with a larger resistivity varied more evidently. For example, the resistivity of sample deposited at 30 °C decreased 2 orders from $6.49 \ \Omega \cdot \text{cm}$ at 50 K to $5.57 \times 10^{-2} \ \Omega \cdot \text{cm}$ at 350 K, while, that of sample deposited at 100 °C just decreased slightly.

Fig. 3. (a) XPS spectra of the a-C films at various deposition temperatures; (b) The change of sp$^2$ content of a-C films with the variation of temperature, and the insert figure exhibits all C 1s peaks of the a-C films.

Fig. 4. (a) Raman spectra; (b) The corresponding fitting results of a-C films deposited at different temperature.
Fig. 5. (a) Cross-sectional TEM image, (b) HRTEM image and corresponding SAED of a-C film deposited at 100 °C.

Fig. 6. Transmittances of the deposited a-C films with the variation of temperatures in different wavelength range (a) 2.5–25 μm and (b) 0.2–1.5 μm; (c) Typical Tauc plot to determine (d) optical bandgap of a-C films at various temperatures.

Fig. 7. (a) I-V characteristic plot and (b) electrical resistivity of the a-C film deposited at different temperature.
from $3.08 \times 10^{-3}$ Ω·cm at 5 K to $1.84 \times 10^{-3}$ Ω·cm at 350 K.

In general, the activation energy ($E_{\text{act}}$) is used to characterize the temperature dependence of conductivity in a-C films, which can be calculated from the Arrhenius law, according to the following formula,

$$E_{\text{act}} = -k\frac{d\ln(\sigma)}{d(1/T)}$$

where $\sigma$ is the conductivity of a-C films, that is the multiplicative inverse of resistivity, $k$ is Boltzmann constant, and $T$ is test temperature [18,48,49]. As shown in Fig. 9(c), the sample with a larger resistivity also exhibited a higher $E_{\text{act}}$, in addition, all $E_{\text{act}}$ of the samples increased mildly with increasing temperature. For instance, from 0.011 eV at 50 K to 0.048 eV at 350 K for the sample deposited at room temperature and from $4.3 \times 10^{-6}$ eV at 5 K to $5.5 \times 10^{-3}$ eV at 350 K for the sample deposited at 100 °C, respectively [18,49], which was usually explained from the broad distribution of band tail states in the a-C films [18].

### 3.5. Discussion

From the optical and electrical properties of a-C films, their transmittance, optical bandgap, resistivity and activation energy exhibited similar tendency with increasing deposition temperature, which can be explained from the evolution of sp$^2$/sp$^3$ ratio and sp$^2$ cluster in the a-C films. Generally, the transmittance and optical bandgap of a-C films decrease with increasing the sp$^2$ content and size of sp$^2$ cluster at relatively low total disordering level [2,42,47]. Namely, the sp$^2$ content and size of sp$^2$ cluster determined the transmittance and optical bandgap simultaneously.

According to XPS, Raman and TEM, it was safe to deduce that, by changing the deposition temperature from 30 °C to 400 °C, the structure of a-C films became much more order, the sp$^2$ content of the films increased; in addition, it was proved that all the a-C films were in the transitional stage from amorphous carbon to nc-G; meanwhile, it might be interpreted that all the sp$^2$ clusters belonged same type since the oxygen content of all the a-C films was very low [15,50]. In general, it could be considered that the size of sp$^2$ clusters decreased with deposition temperature increasing, considering the theoretical model and the variation of photoelectric performance synthetically [31,40].

In this case, as deposition temperature increased to 100 °C, the increase of sp$^2$ contents could be the main factor to cause the decrease of transmittance and optical bandgap, since bond energy of sp$^2$–C is closed to Fermi level which had been proved by amount of computational study [13–15]; however, further increase the deposition temperature to 400 °C, the smaller size of sp$^2$ cluster resulted in the increase of transmittance and optical bandgap, which is the main factor to determine $\pi$ band gap [13]. Similarly, the sp$^2$ content and size of sp$^2$ cluster can also decide the electrical properties of a-C films, by changing transition distances of electrons between clusters [11,12]. When deposition temperature was below 100 °C, the increase in sp$^2$ contents was the main factor to cause lower activation energy and reduced resistivity, at elevated temperature, smaller size of sp$^2$ clusters caused higher activation energy and larger band gap in this relatively stable sp$^2$ content range, as shown in Fig. 10.
4. Conclusion

In summary, by increasing deposition temperature from 30 °C to 400 °C, a-C films with higher sp² content and smaller size sp² cluster can be obtained. As the deposition temperature was below 100 °C, both transmittance and resistivity of a-C films decreased with increasing temperature, which can be explained from the increase of sp² of a-C films. As the deposition temperature increased from 100 °C to 400 °C, both transmittance and resistivity increased with increasing temperature, which was lied on the smaller size of sp² clusters. As a result, this study can provide a route to tune opto-electrical properties of a-C films for its application in amorphous carbon-based optoelectronic devices.

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