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Study of relationship between structure and transmittance of diamond-like carbon (DLC) films

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Abstract: In this paper, the transparent hard diamond-like carbon (DLC) films were deposited on glass substrate by magnetic confined radio-frequency plasma chemical vapor deposition. The structure of films was studied by Raman spectra and X-ray photoelectron spectra (XPS), the transmittance of films by Spectrophotometer. The mechanism of the influence of films structure on transmittance of the films was discussed. The results show that the thickness of films was lower than 100nm, and the transmittance was over 90% in 380－780 nm region. Discussion in theory on the influence of film structure on transmittance was correspondence to experiment results.

Key words: diamond-like carbon films; radio-frequency plasma chemical vapor deposition; structure of the films; transmittance

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1 Introduction

Artificial synthesis of diamond and diamond-like carbon (DLC) have been the advanced and focused research aspect in materials science for about twenty years. As a wear-resistant protective film, diamond-like carbon film has extensive applications. Due to different matrix and service conditions, different requests were proposed to properties and deposition conditions of diamond-like carbon.

There has been many methods to prepare DLC film, however, most of DLC films were not transparent. In 1971, Sol Aisenberg and Ronald Chabot[1] deposited transparent DLC film, which can score glass, at room temperature by ion beam deposition (IBD) method. In 1991, SIEKO Watch Corporation in Japan proposed the idea of taking DLC film as the transparent protective film of the surface of watches. Few reports had been made on production method of large-area depositing transparent DLC film at low temperature and fewer on the study of transmittance of films.

In this paper, radio-frequency plasma glow discharge chemical vapor deposition (RF-PCVD) was used to prepare colorless transparent DLC films under the suitable conditions, and its transmittance was taken a

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preliminary discussion.

2 Experimental methods

DLC films were prepared by homemade magnetic confined radio-frequency glow discharge plasma chemical vapor deposition equipment (*D*650 mm×850 mm). Background vacuum degree was 1.5 Pa, gases used in experiment were industrial dimethylmethane-butane mixing gas, high pure hydrogen (99.99%) and high pure argon (99.99%). Magnetic induction was 0-200 Gs, electrodes were 200 mm×280 mm, and their distance was 50-100 mm, radio-frequency current was 13.56 MHz. Deposition conditions were listed in Table 1.

Table 1 Deposition conditions for colorless transparent DLC films

Conditions	Electrode distance /mm	Electrode voltage /V	rf power /W	Self bias /V	Ar /($cm^3 \cdot min^{-1}$)
Bombardment	50	900	400	220	70
Deposition	50	200	140	100	180
Conditions	H_2 /($cm^3 \cdot min^{-1}$)	C−H /($cm^3 \cdot min^{-1}$)	Magnetic induction intensity/Gs	Chamber pressure /Pa	Time /min
Bombardment	0	0	100	10	3
Deposition	120	3.5	100	25	30

The substrates used in experiments are medicine glass slide, glass of watch and glass of mobile phone screen. SPEX1403 Raman spectrometer was used to study the valence state characteristics of sp^3 and sp^2 carbon in films. ESCA PHI5300 X-ray photoelectron spectrograph (XPS) was used to study valence state of atoms, chemical shift and structure of valence band in films. The transmissivity of DLC film samples in 380-780 nm visible light range were tested by Japanese UV-3101PC spectral photometer.

3 Results and discussion

3.1 Structure of films

Raman spectra of transparent DLC films deposited on glass substrate is shown in Fig. 1, in which the broad peak value appearing at 1560 cm^{-1} and acromion peak appearing at 1300-1400 cm^{-1} show that it own the characteristic of typical amorphous DLC structure, and it can be testified that colourless transparent hard film belong to DLC structure, namely sp^3 structure, which inlay in the sp^2 net structure. The films should be amorphous carbon films containing hydrogen due to the existence of hydrogen during experiment process.

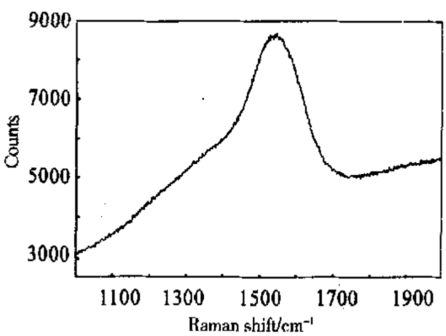

Fig. 1 Raman spectra of the films

Fig. 2 shows the C1s binding energy spectra (XPS) of colourless transparent sample. C1s peak value is 286.9 eV, which shifted to high binding energy direction for over 2 eV, it showed the tendency of the increase of sp^3 configuration. Fig. 3 shows the valence band spectra (XPS). I region (bonding energy 16-21 eV) and II region (bonding energy 10-15 eV) of C1s valence band spectra are close and form the shape of I region main peak and II region acromion peak, III region (bonding energy 3-10 eV) is also apparent, so the spectra characteristic is similar to that of diamond. According to certification of Raman spectra, C1s binding energy spectra and valence band spectra, it can be demonstrated that the structure of this kind of colourless transparent films are amorphous DLC structure with sp^3 configuration.

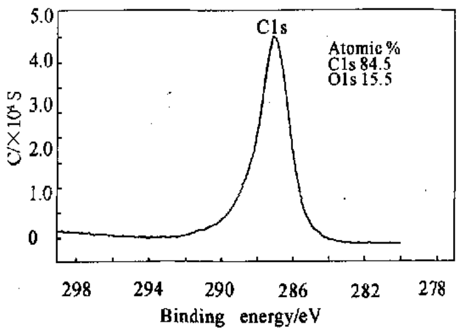

Fig. 2 C1s XPS spectra of the films

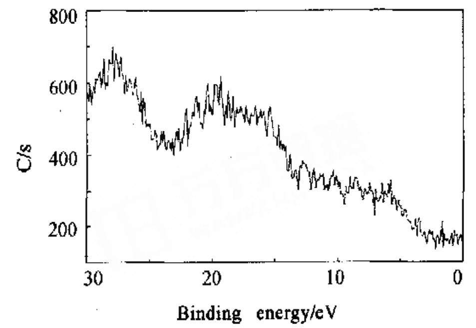

Fig. 3 Valence band XPS of the films

3.2 Transmittance of visible light range

Fig. 4 shows the transmittance curve of filmed glass. Transmittance is over 90% in 380-780 nm region and 91% at 550 nm, respectively. Compared with substrate without film, transmittance decrement is lower than 1%.

3.3 Discussion on structure and colourless transmittance of film

The structure of DLC film is amorphous. Energy band theory of crystalline materials is not adapt to amorphous materials. Research of Mott and Davies[3] showed that in amorphous materials, when a limit was added to the fluctuation of potential field, some allowed energy bands existed, fridge of every allowed energy bands divided, as shown in Fig. 5, which is the energy level figure determined by unbodied characteristic of intrinsic lattice, it has conduction band and valence band with forbidden band (namely migration gap). Thus the crystalline energy band can be introduced to discussed optical characteristics. The relationship between photoabsorption coefficient and optical gap is as follows:

$$\partial h\nu \doteq m(h\nu - E_g) \qquad (1)$$

where ∂ is absorption coefficient, $h\nu$ is photon energy, m is empirical coefficient, E_g is optical gap, namely forbidden band of energy level. When E_g increases, absorption coefficient decreases.

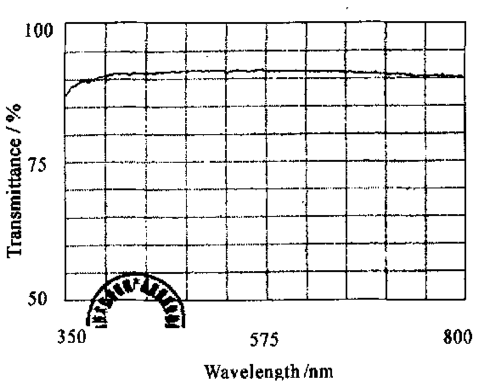

Fig. 4 Transmittance of the films

Dongping Liu[4] proposed as well as J. Roberson did, that E_g value was mainly depended on the structure of π bond formed by sp^2 carbon. If delocalized region formed by π bond was larger, the lower was energy difference of electron transition, as did as E_g. Disorder net-structure of a-C:H film dismutated the structure of sp^2 carbon, this resulted in the covalence between σ and π bond, so E_g was decreased in a large degree. If the content of sp^2 was larger, the possibility of looping of a-C:H film was larger, and E_g was smaller. When the content of sp^2 was certain, the content of H was lower, the looping ability of sp^2 carbon was stronger, E_g was smaller. On the contrary, if the content of H was higher, E_g was larger. So, the content of H had an important influence on the morphology of sp^2 carbon and also on the magnitude of E_g.

From the discussion mentioned above, it can be inferred that if it was requested that light transmission was high, absorption coefficient was small, contrary to E_g, so the content of sp^2 carbon must be small, however, this was related to several parameters matching. When the content of sp^2 carbon was certain, high content of H was correspondent to high content of H in experiment which made it easy to obtain transparent film.

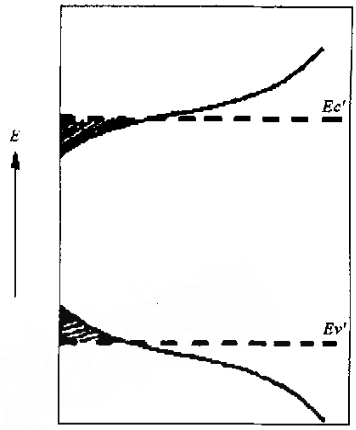

Fig. 5 The state function density of noncrystalline

Since it was requested that films were transparent, the transmittance of light must be high and consistent in full visible light wave band 380 — 780 nm, so the selective absorption was not allowed. Most of research work focused on transmittance of infrared light, maybe the films prepared by most of methods that synthesis DLC was non-transparent with color or black in visible light region, but t transmittance in infrared light region was good.

Wave band in visible light region 380-780 nm was conversed to 3. 27-1. 59 eV by $E=h\nu=h\frac{c}{\lambda}$ (c is light velocity). Many researches obtained the optical gap was $E_g<1.5$eV, so transmittance in infrared light region was good, but in visible light region it was non-transparent. The photon energy of visible light was $h\nu=3.27$-1.59 eV. It was difficult to extend the optical gap of DLC to $1.59\ \mathrm{eV}<E_g<3.27$ eV. Additionlly, E_g was affected by methods and deposition condition. This was the difficulty to prepare colorless transparent a-C:H film. Description mentioned above was considered on intrinsic absorption and did not refer to the influence of impurity and other aspects on absorption. V. Natarajan, *et al.*[5] reported that, although violet and violet-red light can not penetrate, when E_g reached 2. 7 eV, the light whose wave band was over 460 nm can penetrate, this had been a success in some extent. If transmittance in long wave band (600 nm) region of visible light was high, in short wave band (420 nm) it was low and in medium wave band (600—420 nm) decrease gradually, the penetrated light appeared with tawny (see Fig. 6). This was the reason that yellow brown DLC films were obtained in experiments. Because of the $E_g \ll 3.27$ eV, the absorption to visible light always appeared. Since it was requested colorless and transparent, the thickness of the amorphous DLC films must be very small. The thickness obtained in our experiment was lower than 100 nm.

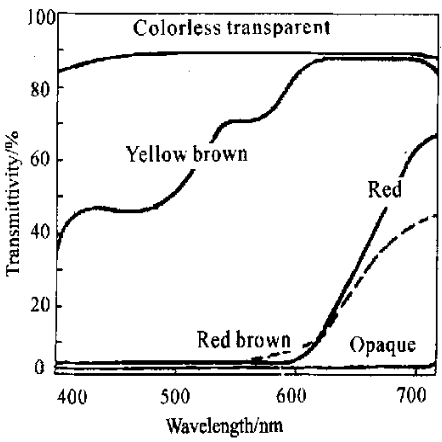

Fig. 6 Color of the mattercorresponding to transmittivity

4 Conclusion

(1) Transparent protective amorphous DLC films were deposited on glass substrate (or plastics) by magnetic confined radio-frequency plasma chemical vapor deposition method. The thickness of films was lower than 100nm, and the transmittance was over 90% in 380—780 nm.

(2) Discussion in theory on the influence of film structure on transmittance was correspondence to experiment results.

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