JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 2, February 2007, p. 379 - 381

Optical properties of PECVD carbon films on silicon subjected to rapid thermal annealing

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Spectral ellipsometry studies have been performed in the range of 400 - 820 nm on hydrogenated amorphous carbon films deposited on c-Si substrates at 340 °C by the 27 MHz plasma decomposition of methanol (CH_3OH) vapor. The films have been subjected to rapid thermal annealing (RTA) at 800 and 1000 °C in vacuum (~10^{-3} Pa). The refractive index and extinction coefficient values of as-deposited films correspond to a polymer-like structure. The decrease of the optical bandgap energy from 3 eV to 1.7 eV caused by RTA suggests a graphitic transformation of the film structure. Selective HF etching of the carbon films has revealed a 4.6 nm thick interfacial region of silicon carbide formed during 1000 °C RTA.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: Hydrogenated amorphous carbon, Plasma enhanced chemical vapor deposition, Silicon carbide interfacial layer, Spectral ellipsometry, Optical constants

1. Introduction

Diamond and diamond-like carbon (DLC) have potential application in the field of optics. They possess unique properties, such as high transparency, high resistance to radiation damage and corrosive environments [1], and a higher laser-damage threshold than common optical coating materials [2] etc.

Hydrogenated amorphous carbon films (a-C:H) have interesting "diamond-like" properties (high hardness, high transparency, high resistivity, and chemical inertness). It has been established [3] that a-C:H films can be doped n- or p-type and, as well as applications as hard, transparent optical coatings and wear-resistant coatings, they can be used as novel semiconducting materials. Films can be deposited using methods such as hydrocarbon gaseous precursor decomposition by plasma-enhanced chemical vapour deposition (PECVD) [4], ion-beam-assisted deposition [5], electron cyclotron resonance plasma deposition [6] etc.

Thin films of a-C:H can also serve as a source for carbonisation of silicon wafers in order to form a buffer layer introduced in SiC technology. Silicon carbide is a wide band-gap semiconductor under development mainly for applications requiring operation at high temperature, high power or high frequency. By a chemical vapour deposition technique high-quality heteroepitaxially grown SiC on Si can be produced. Due to the large lattice mismatch between cubic SiC and silicon, a buffer layer of SiC has been introduced, which is grown by carbonizing the surface of a Si substrate in the CVD system. Carbonization temperatures around 1000-1300 °C produce SiC films with optimum structural properties [7,8]. The chemical conversion of the Si surface region into the SiC interlayer was demonstrated by Nishino *et al.* [9]. The SiC growth has been preceded in ref. [8] by carbonization of Si at temperatures ranging from 1200 to 1340 °C in C_3H_8 and H_2 gas mixtures for a short duration (120-150 s).

Amorphous a-C:H films are in general transparent, smooth and hard films with a wide range of physical and chemical properties strongly dependent on preparation techniques [10]. Information about the optical properties of a-C:H films and a SiC underlayer formed between the film and the Si substrate can be obtained by means of spectral ellipsometry (SE). This method, as a non-destructive and non-contact optical characterization technique, is highly effective for the optical characterization of films. Ellipsometry measures the change in the polarization state of light reflected from the sample, and hence it is very sensitive to any structural alteration in the films caused by technological processes. This change can be represented by ellipsometric angles ψ and Δ through the reflectance ratio of $r_p/r_p = \tan(\psi)\exp(j\Delta)$, where the parameters r_p and r_s are the complex reflection coefficient for light polarized in parallel p and perpendicular s to the plane of incidence. Through computer calculation, the refractive index n, and extinction coefficient k can be determined according to homogeneous thin layer optical theory [11]. Knowing the k values, one can determine the optical bandgap (E_{og}) of films by building a Tauc plot using the equation,

$$(\alpha h\nu)^{1/2} = B(E_{og} - h\nu) \quad , \qquad (1)$$

where B is the density of the localized state constant and α is the absorption coefficient ($\alpha = 4\pi k/\lambda$). The intercept of the linear part of the Tauc plot with the photon energy axis gives the optical bandgap value.

In this paper, we report a spectral ellipsometric study of a-C:H films, deposited by a plasma enhanced chemical vapour deposition (PECVD) process and treated by rapid thermal annealing (RTA). Multi-layer optical models are considered and the influence of the annealing temperature on the optical properties of the formed structures is discussed.

2. Experimental

The a-C:H films were deposited on p-type (100) Si substrates up to a thickness of 108 nm by h.f. (27 MHz) plasma decomposition of methanol (CH_3OH) vapours at a pressure of 10 Pa in a plasma reactor with a parallel electrode configuration. The Si substrate was kept at 340^{o}C during the deposition. The films were subjected to rapid thermal annealing (RTA) at temperatures of 800^{o}C (3 min) and 1000^{o}C (2 min) in vacuum at a residual pressure of ~10^{-3} Pa.

The spectroscopic ellipsometry measurements were performed with a multiple angle Rudolph 436 ellipsometer. The spectral dependences of the ellipsometric angles Ψ and Δ were measured in the range of 400 - 820 nm and at an incident angle of 50^o, while the film thickness was deduced from multiple-angle measurements made at λ=632.8 nm and at angles of incidence ranging from 50 to 60^o with a step of 2^o. The accuracy in determination of the film thickness was ± 0.2 nm, while that of the optical constants was ± 0.005.

Three kinds of samples were measured, namely as-deposited films, RTA treated films and samples with the film etched away in a selective HF etchant after the RTA procedure. The latter aimed to detect an interfacial layer, if it was formed. The ellipsometric measurements were performed after each technological step.

3. Results and discussion

The optical constants of the films were calculated by solving the inverse problem of ellipsometry [11]. It has been shown [7,8] that at temperatures as low as 800 ^{o}C an interfacial layer of SiC cannot be formed. In the case of 800 ^{o}C RTA, this was confirmed by etching away the carbon film from the Si substrate. For these films the SE data analysis could not indicate any top layer on the Si. Therefore, the a-C:H/Si structure for the as-deposited state and annealing at 800 ^{o}C were considered as a single layer-substrate optical system. For the films subjected to 1000 ^{o}C RTA, a double-layer model was used, since at this temperature formation of SiC interfacial layer could be expected and, since further the etching experiments confirmed this.

In Figs. 1 and 2 the dispersion curves of the refractive index *n* and extinction coefficient *k*, respectively, are presented. As is seen, the refractive index has a weak spectral dependence (Fig. 1) and for the as-deposited film the *n* values are around 1.6. This low value of n can be related to a low film density. Similar behavior has been observed for films deposited in a dc glow discharge system [12]. After annealing at 800^{o}C the *n* and *k* values remain close to those for the as-deposited state (Fig. 1 and 2, respectively) indicating that 800^{o}C RTA could not affect the film density much. The extinction coefficient of all the films was negligible over a wide spectral range and below 600 nm it showed a tendency to increase toward shorter wavelengths (Fig. 2).

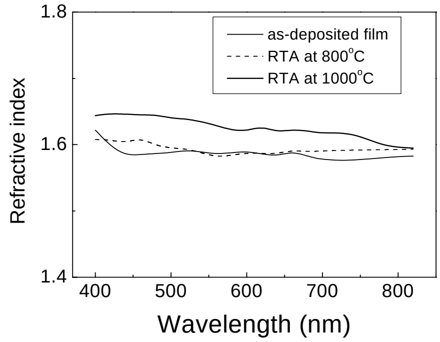

Fig. 1 Refractive index versus light wavelength for as-deposited a-C:H films and after RT annealing at 800 and 1000 ^{o}C.

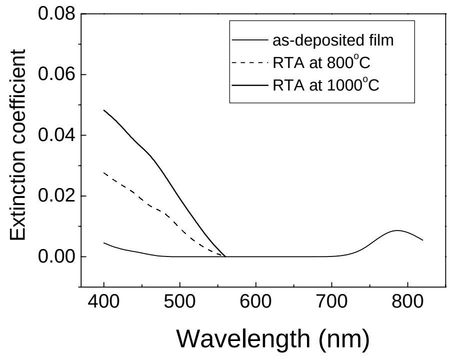

Fig. 2 Extinction coefficient k versus light wavelength for as-deposited a-C:H films and after RTA annealing at 800 and 1000 ^{o}C.

In the case of 1000 ^{o}C RTA, on the etched Si substrate a thin overlayer was detected, which formed during the high temperature annealing. The thickness of this interfacial layer was found to be 4.6 nm. The *n* and *k* values of this layer are given in Fig. 3. From the Tauc plot, the optical bandgap E_{og} value of this layer was deduced and found to be 2.86 eV. The obtained values of the refractive index, extinction coefficient and optical bandgap are similar to those characteristic of SiC thin films [13]. Obviously, carbonization of the Si surface takes place during 1000 ^{o}C RTA and a 4.6 nm thick Si surface layer converts to SiC. Further, in the double-layer model the optical parameters of this SiC interfacial layer were fixed and the optical parameters of the deposited carbon overlayer were the variables in the iteration procedure. The calculated *n* and *k* values as a function of light wavelength are presented in Fig. 1 and 2, respectively. As is seen from Fig. 1, a small increase in the refractive index values is observed, which can be an indication of densification and/or changes in film composition, most probably due to hydrogen loss and/or graphitic transformation to some degree. The latter suggestion was further proved by examination of the optical bandgap energy of these films.

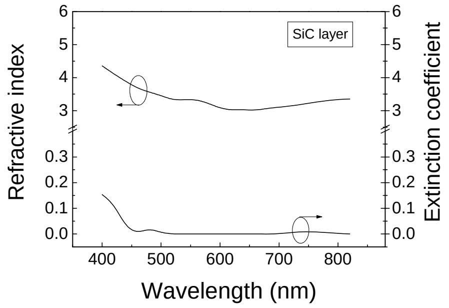

Fig. 3 Spectral dependence of the refractive index and extinction coefficient of the SiC interfacial layer formed during 1000 °C RTA.

From the k values, the absorption coefficient $\alpha=4\pi k/\lambda$ was calculated and the Tauc plot was built. By extrapolating the linear part of the plot to α = 0, the intersection with the energy axis gave the optical bandgap E_{og} of the a-C:H films. The E_{og} values as a function of process temperature are given in Fig. 4.

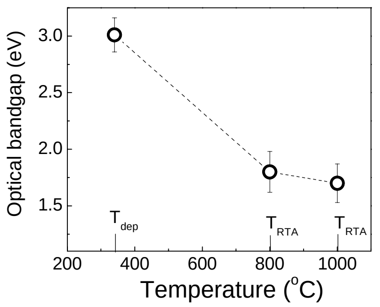

Fig.4. Optical bandgap E_{og} versus process temperature for a-C:H films in the as-deposited state and after RTA at 800 and 1000 °C. The uncertainties in the E_{og} values are showed as error bars.

For the as-deposited film, the E_{og} value is 3.0 eV, which is in good agreement with that reported by Jarman *et al.* [14] for amorphous carbon films prepared using a 13.56 MHz discharge from methane at a pressure of 10.5 Pa on unheated substrates. By the RTA process, the E_{og} value sharply drops to 1.8 eV for a film annealed at 800°C and continues to decrease to 1.7 eV upon increasing the annealing temperature to 1000 °C. This behavior suggests the development of a graphitic transformation of the film structure during annealing [12]. Hydrogenated amorphous carbon films with a polymer-like structure are characterized by a wide optical bandgap ranging from 1.5 up to 4.5 eV and a low refractive index ranging 1.2-1.7 eV, depending on preparation conditions [14-16]. It has been observed that upon increasing the fraction of sp^2 (graphite) carbon content of a-C:H films, the optical bandgap energy significantly decreases [17]. The high value of 1.7 eV for 1000 °C RTA together with the weak refractive index dispersion and low absorption indicates that polymeric-like carbon is still the dominant in our films.

4. Conclusions

Spectral ellipsometric data analysis has revealed that a-C:H films deposited at 340°C by a PECVD technique possess a refractive index of 1.6, negligible absorption over a wide spectral range and an optical bandgap energy of 3 eV, all being characteristics for a less dense and polymer-like film structure. Rapid thermal annealing at 800 and 1000°C leads to the development of a graphitic transformation of the film structure, which is reflected in an increase in the n and k values and a decrease in the optical bandgap to 1.8 and 1.7 eV, respectively. For 1000°C RTA, carbonisation of the Si surface takes place, forming a 4.6 nm thick interfacial SiC layer.

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