Annealing temperature dependence of the optical properties of sputtered hydrogenated amorphous silicon carbide

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Optical measurements (UV-visible-NIR) have been performed at room temperature on sputtered a-SiC:H samples after annealing at temperatures, T_a , between 673 and 973 K. The complex dielectric constant in the range of 0.8-6.5 eV and, using the Wemple-Di Domenico model, the dispersion energy, the Penn gap, the valence electron density, the plasmon energy and the Fermi energy were deduced. The energy gap was determined by means of various models. The decrease of energy gap and the increase of the valence electron density on one hand, and the shift of the exponential absorption edge on the other hand, indicate the coupling of the valence and the conduction band states by optical photon as the annealing temperature increases. Moreover, as T_a exceeds 773 K, the polycrystalline phase can be observed to germinate inside the pre-existing amorphous phase.

1. Introduction

Studies on the physical properties of amorphous silicon carbide a-SiC:H at room temperature after thermal annealing and on hydrogen effusion have been performed recently [1-3]. It has been shown that, for a-SiC:H films deposited by glow-discharge, most of the hydrogen leaves the samples during annealing below 773 K and that the transition from the amorphous state (a-SiC:H) to the polycrystalline state (poli-SiC) occurs at about 923 K.

Above this temperature, the samples become a mixed phase material consisting of sub-micron size crystallites embedded into amorphous matrix. This new-phase material is of interest because of its potential application in thin film devices.

In this paper, we report on a systematic study of the optical properties of annealed a-SiC:H films produced by rf magnetron sputtering. The optical constants were deduced by means of measurements at room temperature in the UV-visible-NIR regions. The annealing temperatures range (673-973 K) has been chosen to scan the hydrogen effusion and phase transition from amorphous to crystalline form.

A careful analysis of the optical constants allowed us the determination of some characteristic parameters of the material.

2. Experimental details

The films were deposited by rf magnetron sputtering. The deposition parameters were: Ar flow rate 100 sccm, CH₄ flow rate 1.5 sccm, pressure 1.6 Pa, substrate temperature 200 °C. The films have a thickness varying in the range 0.16–0.18 μ m. The only variable was the power density which was varied from 0.6 to 1.6 W cm⁻².

Isocronal annealing was carried out for 1 h in vacuum (10^{-2} Pa) at annealing temperatures, T_a , varying between 673 and 973 K.

The refractive index, the absorption coefficient, and the real and imaginary part of the dielectric constant were obtained from transmittance and reflectance measurements performed with a Perkin-Elmer UV-visible NIR Lambda 9 spectropho-



Fig. 1. ϵ_1 vs. photon energy, E, for (a) SP250 sample and for (b) SP100 sample.

tometer. The extraction of the optical constants was made following a procedure described elsewhere [4].

A Hitachi S2700 scanning electron microscopy (SEM) at variable magnification was used to observe the film structure.

The samples are labeled SP followed by a number indicating the total power in watt.

3. Results

In figs. 1(a) and (b) the real part of the dielectric constant, ϵ_1 , for the samples SP250 and SP100,

respectively, is plotted vs. photon energy for various annealing temperatures, T_a . The variation of $\epsilon_1 = n^2 - k^2$ with photon en-

The variation of $\epsilon_1 = n^2 - k^2$ with photon energy and annealing temperatures essentially reflects the behaviour of n^2 since $n \gg k$ for these films.

We observe that the values of ϵ_1 are higher for the sample richer in silicon and, for both, they increase with T_a. As the ratio Si/C (obtained by means of nuclear techniques) increases, a shift of the energy corresponding to ϵ_{1max} towards lower energies is observed. This energy is 4.6 eV and 5.3 eV, respectively, for samples SP250 and SP100.

The values of $\epsilon_{1\text{max}}$ are reported in table 1. The

Table I	
Optical	parameters

Sample	T _a (K)	Si/C	€ _{1max}	€ _{2max}	E _m (eV)	E _d (eV)	$\hbar \omega_{\rm p} ({\rm eV})$ (eV)	$n_{\rm v}$ (10 ²³ e/cm ³)	E _F (eV)
SP250	as deposited	2.8	20.0	10.3	5.3	45.6	12.4	1.1	8.4
	627		22.7	11.2	5.3	47.7	12.7	1.2	8.7
	727		25.2	12.4	5.4	51.8	13.4	1.3	9.4
	827		26.5	13.4	5.5	56.3	14.1	1.4	10.0
	927		27.9	14.2	5.5	57.2	14.2	1.5	10.1
SP100	as deposited	2.2	14.4	10.0	4.7	22.0	11.1	0.9	7.2
	627		16.6	11.4	4.8	25.1	11.8	1.0	7.9
	727		17.6	12.9	4.9	28.2	12.7	1.2	8.7
	827		18.1	13.6	5.0	30.8	13.4	1.3	9.3
	927		18.3	15.2	5.2	38.7	15.3	1.7	11.2

corresponding values for a-Si, c-Si and c-SiC are, respectively, 2.7 eV [5,6], 3.3 eV [5,7] and 6.4 eV [8].

From the experimental values of the $\epsilon_1(E)$, we resort to an evaluation of the spectroscopic parameters: the dispersion energy, E_a , and the average excitation energy, E_d , almost equal to the Penn gap [4].

4. Discussion

According to the model of Wemple-Di Domenico [10] we have

$$\epsilon_1(E) = 1 + \frac{E_d E_m}{E_m^2 - E^2}.$$
(1)

A plot of $(\epsilon_1(E) - 1)^{-1}$ vs E^2 yields the values of E_d and E_m reported in table 1. We observe that our experimental results for E_d are in agreement with Wemples's contention of the dependence of E_d on the short range order and are comparable to that of crystalline silicon for the sample rich in silicon at temperatures below the crystallization temperature, T_c . Above this temperature, the values increase.

By contrast, the results on the sample less rich in silicon show values of E_d lower than that of c-C (49.7 eV). These lower values can be explained by the presence, in the sample, of carbon in graphitic-like rather than in diamond-like form. However E_d increases with T_a approaching the values (42 eV) of c-SiC at temperatures above T_c .

The average excitation energy, $E_{\rm m}$, is related to the plasma frequency, $\hbar \omega_{\rm p}$, and then to the plasmon energy by the relationship [9]

$$\epsilon(0) - 1 = (\hbar\omega_{\rm p})^2 / E_{\rm m}^2$$
⁽²⁾

and $(\hbar \omega_p)^2$ is directly related to the density of valence electrons n_y by

$$\left(\hbar\omega_{\rm p}\right)^2 = \hbar^2 e^2 n_{\rm v}/m\epsilon_0, \tag{3}$$

where the symbols have their usual meanings.

From eqs. (1)-(3) we deduce

$$n_{\rm v} = \frac{m\epsilon_0}{\hbar^2 e^2} \frac{E_{\rm m}^2}{\epsilon(0) - 1} \,. \tag{4}$$

Making use of values of $E_{\rm m}$, we calculate the values of $n_{\rm v}$ and the plasmon energy $\hbar \omega_{\rm p}$ reported in table 1.

It is known that optical transitions in amorphous semiconductors, as in their crystalline counterpart, can be treated as one electron excitation. Such transitions require the absorption of a photon and contribute to the imaginary part of the complex dielectric constant, ϵ_2 , since it represents the absorptive part of such constant.

In figs. 2(a) and (b) the dependence of ϵ_2 on photon energy for the same samples as in figs. 1(a) and (b) is plotted. The values of ϵ_2 are reported in table 2.



Fig. 2. ϵ_2 vs. photon energy, *E*, for (a) SP250 sample and for (b) SP100 sample.

Table 2 Energy gap and slope

Sample	<i>T</i> _a (K)	ε2		$(\epsilon_2 E^2)^{1/2}$		$(\epsilon_2 E)^{1/2}$	
		$\overline{E_{g} (eV)}$	$\beta (eV)^{-1}$	$\overline{E_{g}(eV)}$	β	$\overline{E_{g}(eV)}$	$\beta (eV)^{-1/2}$
SP100	as-deposited	2.55	7.42	2.20	6.90	2.12	3.34
	627	2.46	8.23	2.13	7.31	2.09	3.54
	727	2.33	8.70	2.05	7.50	1.93	3.70
	827	2.18	9.81	1.97	7.91	1.77	3.74
	927	2.07	9.87	1.87	7.85	1.63	3.74
SP250	as-deposited	2.15	4.40	1.95	6.30	1.73	2.98
	627	2.15	4.58	1.94	6.00	1.72	2.95
	727	2.13	4.70	1.91	5.81	1.69	2.86
	827	2.09	4.69	1.87	5.57	1.64	2.67
	927	2.04	5.14	1.82	5.72	1.59	2.68

Since the area under the curves of ϵ vs. *E* is a measure of the total absorption, the increase of ϵ_2 and of the quoted area as T_a increases indicate an increase of the valence band density of states. This increase is in agreement with the values of n_v obtained by the relationship

$$n_{\rm v} = \frac{8\pi m\epsilon_0}{h^2 e^2} \int_0^{E_{\rm max}} \epsilon_2(E) E \, \mathrm{d}E, \qquad (5)$$

where E_{max} is the energy corresponding to $\epsilon_{2\text{max}}$.

The values of n_v as calculated from eq. (5) are the same, within experimental errors, as those obtained from eq. (4) and reported in table 1. When n_v is known, the Fermi energy, E_F , can be evaluated from the relationship.

$$E_{\rm F} = \frac{k^2}{2m} \left(3\pi^2 n_{\rm v} \right)^{2/3}.$$
 (6)

The calculated values of $E_{\rm F}$ are reported in table 1.

The Fermi energy increases slowly to a value about constant for temperatures corresponding to the polycrystalline form of the more silicon rich sample. In the sample with less silicon, $E_{\rm F}$ increases sharply due to the effect of carbon content.



Fig. 3. Absorption coefficient, α , vs. photon energy, E, for (a) SP250 sample and for (b) SP100 sample.

In figs. 3(a) and (b) the absorption coefficient, α , is plotted vs. energy. Since in the fundamental absorption region the absorption is due to transitions from the top of valence band to the bottom of the conduction band, an increase of density of state in the valence band with increase in annealing temperatures (see table 1) shifts the absorption edge to lower energies. Such a shift to lower energies with the annealing temperature is similar to that of c-Si absorption edge [11,12]. It is significant to note the sharp variation of α when T_a is greater than the crystallization temperature, T_c .

The experimental values of ϵ_2 and α lead us to evaluate the optical gap. It is found [5,13,14] from theoretical considerations that a function of energy of the form

$$f(E) = \epsilon_2(E)^{\tau} E^{\sigma} \tag{7}$$

can be used to determine the optical gap for amorphous semiconductors. The τ and σ parameters depend on the choice of the form of the bands and of the transitions matrix element.

The optical gap is deduced from the intersection of the straight line of the linear trend of the function with the energy axis.

Taking into account our results we have examined the following expressions for f(E):

$$f_1(E) = \epsilon_2(E), \tag{8}$$

$$f_2(E) = \left[\epsilon_2(E)E\right]^{1/2},\tag{9}$$

$$f_3(E) = \left[\epsilon_2(E)E^2\right]^{1/2}.$$
 (10)



Fig. 5. Static refractive index, n_0 , vs energy gap, E_g .

The first model assumes linear bands, constant dipole matrix element and direct transitions between extended states in the valence and conduction bands. The model represented by eq. (9) considers indirect allowed transitions under the assumption of parabolic bands. Finally eq. (10) is the well known Tauc formula. The model assumes parabolic bands and constant momentum matrix element. The values of the extrapolated gaps and the relative slopes are reported in table 2. The gaps of our as deposited films are comparable to those obtained by many authors for rf-sputtered films.

After annealing, we note a decrease in the optical gap at temperatures above 673 K which indicates an irreversible process and may be mainly attributed to the loss of hydrogen. At tempera-



Fig. 4. (a) Energy gap, E_g , vs. annealing temperature, T_a , for SP250 and SP100 samples. (b) Slope, β , vs. annealing temperature, T_a , for SP250 and SP100 samples.

tures above T_c a decrease of E_g is observed, whereas the slopes, β , become constant.

The trends of E_g vs. T_a , obtained by means of the three examined models, are plotted in fig. 4(a). In fig. 4(b) the slope β vs. T_a obtained by the Tauc model is plotted.

From the Kramers-Kronig relationship [15,16] written for E = 0, we have

$$\epsilon_1(0) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(E)}{E} dE.$$
(11)

Since for $E < E_g$, $\epsilon(E) = 0$, the inferior limit of the integral becomes E_g . Taking into account that $\epsilon_1(0) = n_0^2$, where n_0 is the static refractive index, eq. (10) relates n_0 and E_g . In fig. 5 n_0 vs. E_g is plotted. The interpolation of experimental data gives a linear relationship, the analytic expression of which is

 $n_0 = 7.5 - 2.5E_{\rm g}$ (sample SP250), (12)

$$n_0 = 8 - 2.5E_g$$
 (sample SP100). (13)

The slope, $dn_0/dE_g = 2.5 \text{ eV}^{-1}$, is the same for the two samples.

A scanning electron micrograph for the sample SP250 annealed at 973 K, in which microcrystals distributed in an amorphous matrix can be observed is shown in fig. 6. The submicron crystals present at 673 K tend to conglomerate giving rise to a microcrystals distributed in the amorphous matrix.



Fig. 6. Scanning electron micrograph for SP250 sample annealed at 973K.

5. Conclusions

Increasing T_a results in the coupling of the valence and conduction band states by optical photons as well as in the progressive evolution to a phase characterized by the presence of a polycrystalline state in an amorphous matrix. These considerations can be justified by the following experimental results:

(1) the continuous increase of the real and imaginary part of the dielectric constant through out the examined spectral range.

(2) the increase of the dispersion energy, the Penn gap, the plasmon energy, the Fermi energy and the valence electron density.

(3) the trend of the optical energy gap vs. T_a (light decrease and saturation above 873 K independently of the theoretical model used for its calculation).

(4) the shift of the absorption edge.

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