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Thermal Modification of a-SiC:H Films Deposited by Plasma Enhanced Chemical Vapour Deposition from CH_4+SiH_4 Mixtures *

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The effects of thermal annealing on photoluminescence (PL) and structural properties of a-$Si_{1-x}C_x$:H films deposited by plasma enhanced chemical vapour deposition from CH_4+SiH_4 mixtures are studied by using infrared, PL and transmittance–reflectance spectra. In a-SiC:H network, high-temperature annealing gives rise to the effusion of hydrogen from strongly bonded hydrogen in SiH, SiH_2, (SiH_2)n, SiCHn and CHn configurations and the break of weak C−C, Si−Si and C−Si bonds. A structural rearrangement will occur, which causes a significant correlation of the position and intensity of the PL signal with the annealing temperature. The redshift of the PL peak is related to the destruction of the confining power of barriers. However, the PL intensity does not have a significant correlation with the annealing temperature for a C-rich a-SiC:H network, which refers to the formation of π-bond cluster as increasing carbon content. It is indicated that the thermal stability of C-rich a-$Si_{1-x}C_x$:H films is better than that of Si-like a-$Si_{1-x}C_x$:H films.

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Films of a-SiC:H have been receiving much attention as wide band gap optoelectronic materials which are compatible with standard silicon technology.[1−4] As a promising material, their thermal stability is very important. To study the thermal stability of a-SiC:H films, we select a set of a-$Si_{1-x}C_x$:H films with different carbon content. A cycle annealing process is applied to a-SiC:H films with increasing temperature. The microstructure of the films will be modified, which will directly affect their optical properties. The infrared (IR) spectra are used to characterize the change of chemical bond configurations. The transmittance−reflectance (T–R) spectra in the UV-visible near-infrared range are used to explore the change of a-SiC:H network with the increase of annealing temperature. In order to study further the effect of annealing on photoluminescence (PL), the PL spectra are measured for a-SiC:H films with different carbon content. A completely different PL behaviour for C-rich and Si-like a-SiC:H films is found. The related physics mechanism is discussed.

Films of a-SiC:H were deposited by the plasma enhanced chemical vapour deposition (PECVD) system from SiH_4+CH_4 mixtures with an rf power of 4 W, an electrode distance of 14 mm, a deposition pressure of 60 Pa and a substrate temperature of 180°C. The film thickness was in the range $0.9-1.1\,\mu$m. Films were deposited onto different substrates suitable for different measurements. The uniformity of the deposition was tested by a Mary-102 type ellipsometer (1 mW He–Ne laser, $\lambda = 632.8$ nm) and the thickness was found to vary within 3−5% over the 45 cm^2 silicon wafer. In order to obtain the optical gap (E_g) values, the optical absorption coefficients in the wavelength range 200−3200 nm (6.2−0.38 eV) have been obtained from T–R spectroscopy by a Perkin–Elmer Lambda 10 spectrophotometer. The bonding configuration has been studied by an FTIR Perkin–Elmer 2000 spectrophotometer with a resolution of 4 cm^{-1} in the range 400–4000 cm^{-1}. The absorption coefficient was deduced from the recorded IR spectra taking into account the absorption in the silicon substrate and the influence of interference fringes. The integrated intensities of the deconvoluted peaks were calculated for the different vibration modes. The PL spectra have been measured at room temperature using a JY800 spectrometer with a 300 mW Ar$^+$ laser at 514.5, 488.0 and 457.9 nm. Isochronal annealing was carried out on the a-SiC:H films for 30 min in vacuum (10^{-2} Pa) at annealing temperatures varying between 250–500°C.

Fig. 1 shows the IR absorption spectra of a-SiC:H films deposited by PECVD from the CH_4+SiH_4 mixtures and the peak ascription. To understand the behaviour of the different bonding configurations as a function of the annealing temperature for the a-SiC:H films with different carbon content, we show the integrated intensities of different IR modes as a function of the annealing temperature. Fig. 2(a) shows the integrated intensity of the IR mode at 630 cm^{-1}, attributed to the Si−H wagging vibration, as a function of the annealing temperature. The integrated intensity decreases with the increase of the annealing temperature. Fig. 2(b) shows an increase for the integrated intensity of the IR mode at 670 cm^{-1}, attributed to the Si−C stretching vibration, as a function of the annealing temperature. Fig. 2(c) shows a decrease for the integrated intensity of the mode of $780-800$ cm^{-1}, attributed to the rocking or wagging vibrations of CH_3 radical attached to Si or Si–C, as a function of the annealing temperature.[5] The IR peak at 2100 cm^{-1} can be deconvoluted into 2120 and

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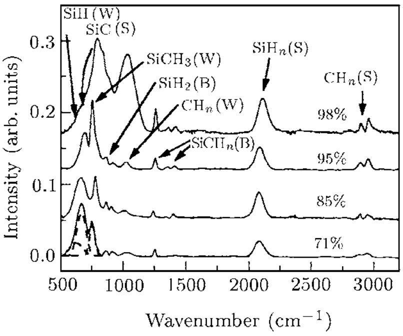

Fig. 1. IR absorption spectra of a-SiC:H films as a function of CH_4 fraction: (W) wagging; (S) stretching; (B) bending.

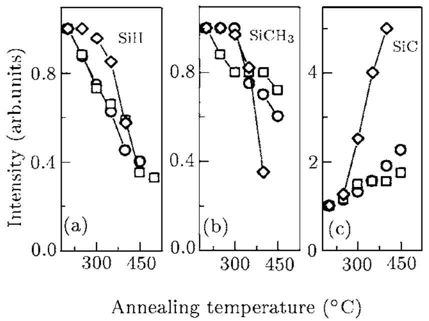

Fig. 2. IR integrated intensities of the deconvoluted peaks as a function of annealing temperature for the Si–H and SiCH wagging vibration at 630 $cm^{-1}$and 780 cm^{-1}, and the Si–C stretching vibration at 680 cm^{-1}: ○, sample A; □, sample B; ◇, sample C.

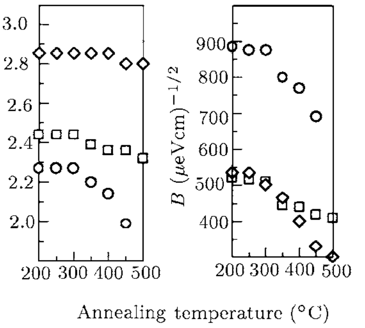

Fig. 3. Values of E_g and B as a functions of the annealing temperature: ○, sample A; □, sample B; ◇, sample C.

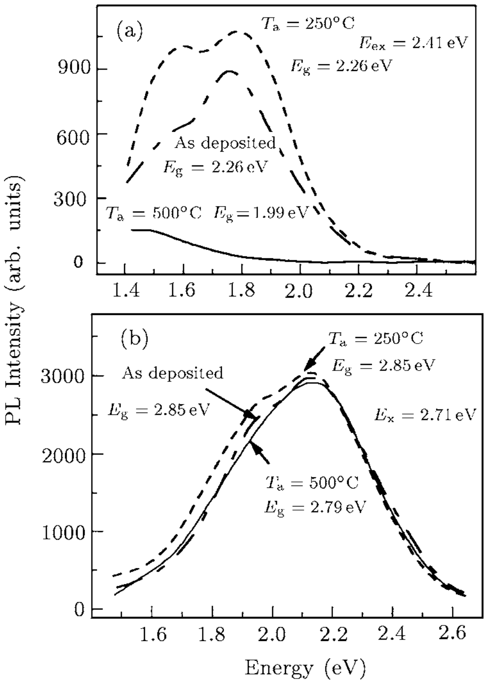

Fig. 4. PL spectra as a function of annealing temperature for (a) sample A (C/(C+Si)=0.21) and (b) sample C (C/(C+Si)=0.34).

2065 cm^{-1} peaks. The peak at 2120 cm^{-1} was attributed to the vibration of the silicon atom bound with hydrogen atoms in a dihydride configuration and lying at the internal surface of the voids in the film.[5−8] Our experimental results indicate that the IR peak at 2100 cm^{-1} shifts to 2080 cm^{-1} for an annealing temperature greater than 400°C, which suggests that those hydrogen atoms in a dihydride configuration are unstable at high temperatures. The integrated intensity of the IR mode at 2850 − 3050 cm^{-1}, attributed to the stretching vibrations of the CH_n group in both sp^3 and sp^2 configurations,[7] decreases with the increasing annealing temperature, which indicates that CH_n groups are unstable under high-temperature annealing.

The IR integrated intensities of SiH_n, $SiCH_3$ and CH_n groups decrease with the increasing annealing temperature, which suggests that hydrogen effusion occurs. Films of a-SiC:H can be regarded as carbon incorporated into a-Si:H, which leads to two effects. One effect is the new defect induced by carbon entering into the network; the second is the formation of the SiCH and CH_n configurations. The existence of new units is a major reason to produce more microvoids in a-SiC:H than in a-Si:H networks. As the hydrogen effuses from network, many dangling bonds related to silicon and carbon are created. Furthermore, the weak C−C, Si−Si, and C−Si bonds will be broken and a new structural rearrangement will occur. As a result of this, the IR integrated intensity of the Si–C stretching mode at 670 cm^{-1} has a significant increase with the increase of the annealing temperature.

Table 1. Elemental composition and E_g of a-SiC:H films deposited from SiH_4CH_4 plasmas with different methane percentage, $Y(CH_4)=[CH_4/(SiH_4+CH_4)]$.

Sample	$Y(CH_4)$	C/(C+Si)	C (at.%)	Si (at.%)	H (at.%)	E_g (eV)
A	0.85	0.21	10.5	41.1	48.4	2.27
B	0.95	0.34	18.2	35.3	46.5	2.45
C	0.98	0.50	27.9	27.9	44.2	2.85

The optical Tauc gap (E_g) was obtained by T–R measurements. E_g was determined by extrapolating the function $(\alpha E)^{1/2} = B(E - E_g)$ to $\alpha(E) = 0$, where α is the absorption coefficient and B is the constant proportional to the optical joint density of states.[9] We select a-SiC:H samples from Si-like to C-rich with carbon content from 10.5 to 27.9%, as given in Table 1. The change is also confirmed by the abrupt reduction in the Tauc slope B from the Si-like value 885 $cm^{-1/2}$ $eV^{-1/2}$ to the C-rich value of 535 $cm^{-1/2}eV^{-1/2}$.[10] The E_g and B values as functions of annealing temperature are shown in Fig. 3, where these values are approximately constant for a-SiC:H films at low-temperature annealing. However, they are dramatically decreased for Si-like a-SiC:H films with an annealing temperature greater than 350°C. The decrease of the B value with the increase of the annealing temperature can be explained by some increase in the disorder of the structure.[11] It is clear in Fig. 3 that the E_g and B values become stable for the annealing temperature with the increase of carbon content. In other words, the thermal stability of the a-SiC:H film increases with the increase of the carbon content.

Fig. 4(a) shows the PL spectra for a-SiC:H films with different carbon content at different annealing temperatures. For the low carbon a-SiC:H films ($E_g <$ 2.5 eV), the PL intensity increases at a 250°C annealing temperature, then the PL intensity is quenched by the high-temperature annealing process. However, the PL intensity is almost constant for C-rich a-SiC:H films at different annealing temperatures. To interpret these results, a multiphase network structure for a-SiC:H films was proposed. The IR results supply a support for multiphase networks, in which the a-SiC:H amorphous networks consist of SiH, SiH_2, SiC, $SiCH_3$ and CH_n groups in sp^2 and sp^3 carbon configurations. Roberston[12] had calculated the densities of states (DOS) of Si, SiH, SiC, SiCH, CH and C in sp^2 and sp^3 configurations. According to Bradsk's quantum well model,[13] we tentatively divide them into two phases based on the theoretical results.[12] One is the quantum well region composed of a-Si, a-SiC or sp^2 C cluster (in C-rich a-$Si_{1-x}C_x$:H films). As carbon atoms enter into the a-Si:H network, the SiC, CH_n and SiCH phases or sp^3 sites (in C-rich a-$Si_{1-x}C_x$:H films) will increase. Owing to a quantum confinement effect, the larger barrier height of SiHCH, CH_n and C in sp^3 phase results in a higher ground energy for electrons in the well compared with SiH in the a-Si:H network. As a result, the PL peak gives a blueshift with the increase of the carbon content. When the films of Si-like a-SiC:H are annealed at 250°C, structural relaxation and reconstruction occur, which results in a decreasing defect density. These defects are correlated with nonradiative recombination centres.[14] Thus, the PL intensity has a small increase compared with the as-deposited sample. At high-temperature annealing, the PL intensity decreases, and the PL peak shifts to the low-energy side (redshift) for the Si-like a-SiC:H films. When the annealing temperature reaches 500°C, the luminescence peak on the high-energy side disappears, and only the lower PL peak at 1.5 eV can be observed. This is due to hydrogen effusion from SiH_2, SiCH and CH_n groups, resulting in a decrease in the content of SiH_2, SiCH and CH_n, so that the confining action of barrier becomes weak. Thus, the ground-state energy of electrons in the wells will decrease. Furthermore, as the annealing temperature increases, defects increase because of hydrogen effusion, which will give rise to increasing nonradiative recombination centres, resulting in PL signal quenching.

As the annealing temperature increases, the PL intensity is almost constant for C-rich a-SiC:H films, as shown in Fig. 4(b), which is a completely different PL behaviour from the Si-like a-SiC:H films. For C-rich a-SiC:H films, the concentration of the CH_n, SiCH and SiH_n groups will decrease with the increase of the annealing temperature, so the confining action of the barrier regions becomes weak. Moreover, the defect density increases with the increasing annealing temperature due to hydrogen effusion from CH_n, SiCH and SiH_n groups. These lead to the PL redshift and to the PL intensity decrease. However, almost constant PL intensity is experimentally observed, which indicates that the annealing process does not significantly affect the PL signals. For the C-rich a-SiC:H films, carbon atoms dilute tetrahedral coordinated sp^3-bonded networks, where the carbon atoms have a tendency to form planar coordinated sp^2 sites in C-rich alloys.[15] The presence of π clusters has a pronounced effect on the luminescence properties of C-rich a-SiC:H alloys.[4] In σ-bonded amorphous semiconductors such as a-Si, transitions from localized to localized (L–L) states are generally forbidden, because there is little overlap between the initial and the final states which tend to be localized in different regions of real space.[12] In the π-bonded clusters, the valence- and conduction-band states are localized in the same part of real space. These states now have a significant overlap so that these L–L transitions are allowed. As π-bonded clusters form in C-rich a-SiC:H alloys, the overlap integral of L–L states increases with the increase of π-bonded clusters. This may account for the difference of the PL behaviours between Si-like and C-rich a-SiC:H alloys. The independence of PL intensity from the annealing temperature for C-rich a-SiC:H films suggests that the luminescence is associated with clusters as a largely intra-cluster process.

In conclusion, the thermal stability of a-$Si_{1-x}C_x$:H films increases with the increase of carbon content, as confirmed by the dependence of the E_g and B values on the annealing temperature. As carbon atoms enter into the a-Si:H network, the SiH_n, SiC, CH_n and SiCH phases or sp^3 sites (in C-rich a-$Si_{1-x}C_x$:H films) will increase, which leads to increasing quantum confinement action for the electrons in a quantum well. The annealing process will lead to the effusion of hydrogen from SiH_n, CH_n and SiCH groups, causing the decreasing quantum confinement action. The PL peak shifts to the lower-energy side with the increase of annealing temperature and the PL intensity is strongly correlated with defects for Si-like a-$Si_{1-x}C_x$:H films. However, the PL intensity is almost constant for the C-rich a-SiC:H films with the increase of annealing temperature, which suggests that the luminescence is associated with clusters as a largely intra-cluster process.

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