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Thermal modification of wide-bandgap hydrogenated amorphous silicon–carbon alloy films grown by plasma-enhanced chemical vapour deposition from C_2H_2+SiH_4 mixtures

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ABSTRACT

The thermal stability of hydrogenated amorphous silicon–carbon (a-$Si_{1-x}C_x$: H) alloy films grown by plasma-enhanced chemical vapour deposition from C_2H_2+SiH_4 mixtures was characterized by means of infrared spectroscopy, electron spin resonance, transmittance–reflectance spectroscopy and photoluminescence (PL) spectroscopy. It is demonstrated that the network undergoes relaxation and reconstruction under the condition of low-temperature annealing. Weak C–C, Si–Si and C–Si bonds will be broken, and a new stage of hydrogen effusion and structural rearrangement will occur under the condition of high-temperature annealing. The thermal stability a-$Si_{1-x}C_x$: H of films increases with increase in carbon content. In carbon-poor a-$Si_{1-x}C_x$: H networks, the dangling bonds are the main non-radiative recombination channel, which causes a strong correlation of the PL signal with defect density. In carbon-rich a-$Si_{1-x}C_x$: H networks, π-bonded clusters play an important role in the luminescence process. The PL intensity has little dependence on defects in carbon-rich a-$Si_{1-x}C_x$: H.

§ 1. INTRODUCTION

Wide-bandgap carbon-rich intrinsic hydrogenated amorphous silicon–carbon (a-$Si_{1-x}C_x$: H) alloy films are interesting materials for optoelectronic devices such as light-emitting diodes (LEDs) and colour sensors (Tawada, Kondo, Okamoto and Hamakawa 1982, Chang, Chang, Fang and Jwo 1987, Demichelis *et al.* 1993, 1994). The incorporation of carbon in the amorphous silicon network gives the possibility of tuning the bandgap of a-$Si_{1-x}C_x$: H in the range from 1·7 to 3·5 eV, although the presence of carbon induced defect states in the gap degraded the optoelectronic properties of the materials (Demichelis *et al.* 1993). Device-quality films of a-$Si_{1-x}C_x$: H with an energy gap below 2·3 eV can be deposited by the plasma-enhanced chemical vapour deposition (PECVD) technique under suitable plasma conditions from CH_4+SiH_4 mixtures (Demichelis *et al.* 1994).

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On the other hand, the application of a-$Si_{1-x}C_x$: H films in LEDs and coating technology has increased the interest in materials having energy gaps higher than 2·5 eV. The carbon incorporation from CH_4 is not efficient because of the high dissociation energy of the CH_4 molecule. A methane fraction exceeding the 95% is needed to get a carbon content higher than 50%, so that the plasma chemistry of CH_4 is not suitable for easy control of the deposition process, even if high-bandgap a-$Si_{1-x}C_x$: H films have been obtained by PECVD in the 'low-power regime' with low deposition rates (Solomon, Schmidt and Tran-Quoc 1988a, Solomon, Schmidt, Senemaud and Khodja 1988b). However, wide-bandgap a-$Si_{1-x}C_x$: H films have been produced with high deposition rates using new sources of SiH_4 and hydrocarbons such as acetylene, ethylene and tetramethylene (Matsuda *et al.* 1980, Lin and Feldman 1983, Akita, Nakayama, Yamano and Kawamura 1989a, Akita, Wakita, Nakayama and Kawamura 1989b).

The thermal stability of a-$Si_{1-x}C_x$: H is very important in applications and, in particular, the thermal stability of the luminescence is essential for optoelectronic devices. So the influence of annealing on the luminescence properties must be studied in both physics and applications. In order to investigate the thermal stability of wide-bandgap a-$Si_{1-x}C_x$: H films grown by PECVD from C_2H_2+SiH_4 gas sources, we chose a-$Si_{1-x}C_x$: H films with different carbon contents as experimental samples. A cyclic annealing process is applied to a-$Si_{1-x}C_x$: H films using increased temperatures. The microstructure of the films will be modified, which will directly affect the optical and electrical properties. The infrared spectra are used to characterize the bonding configuration change with increasing annealing temperaure. By evaluating the electron spin resonance (ESR) line shape, the defect properties are characterized. In order to investigate further the influence of annealing on optical properties, photoluminescence (PL) spectra and transmittance–reflectance (T–R) spectra with respect to annealing temperature are measured for different a-$Si_{1-x}C_x$: H films with different carbon contents. Completely different PL behaviour is found for a-$Si_{1-x}C_x$: H films with different carbon contents. The thermal stability of a-$Si_{1-x}C_x$: H films are characterized. The modification of the a-$Si_{1-x}C_x$: H structure by thermal annealing and related physical mechanisms are given.

§ 2. Experimental details

The a-$Si_{1-x}C_x$: H films were deposited by using an ultra-high-vacuum PECVD system with SiH_4+C_2H_2 mixtures. The deposition parameters were optimized to obtain device-quality films (Demichelis, Giorgis, Pirri and Tresso 1995b). The film thicknesses were in the range of 0·5–1·2 μm. The films were deposited onto different 10 cm^2 substrates suitable for different measurements. The uniformity of the deposition was tested by interferometric measurements, and the thickness was found to vary within 10% over the whole area. The determination of absolute silicon and carbon contents was performed using the Rutherford back-scattering technique. The elastic recoil detection analysis technique was used to determine the absolute hydrogen content. In order to obtain the optical gap and E_{04} values, the optical absorption coefficients in the wavelength range 200–2500 nm were obtained from T–R spectroscopy with a Perkin–Elmer Lambda 9 spectrophotometer. The bonding configuration was studied with a Fourier transform infrared Perkin–Elmer 2000 spectrophotometer operating in its absorption mode in the range 400–4000 cm^{-1}. The absorption coefficient was deduced from the recorded infrared 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 were measured at room temperature using a J-Y800 Raman spectrometer and a 300 mW Ar^+ laser at 514·5 nm and 457·9 nm and a N_2 laser at 337·1 nm. Isochronal annealing was carried out on the a-$Si_{1-x}C_x$: H films for 30 min in vacuum (10^{-2} Pa) at annealing temperatures varying between 250 and 500°C. The ESR measurements were performed with a Varian EPR-109 spectrometer. Both g values and the intensity of the spin resonance signal of the samples were measured by comparison with calibrated spectra obtained from a 1,1-dyphenil-2-pyry(hydrazil) sample and Varian pitch ($g = 2{\cdot}0029$).

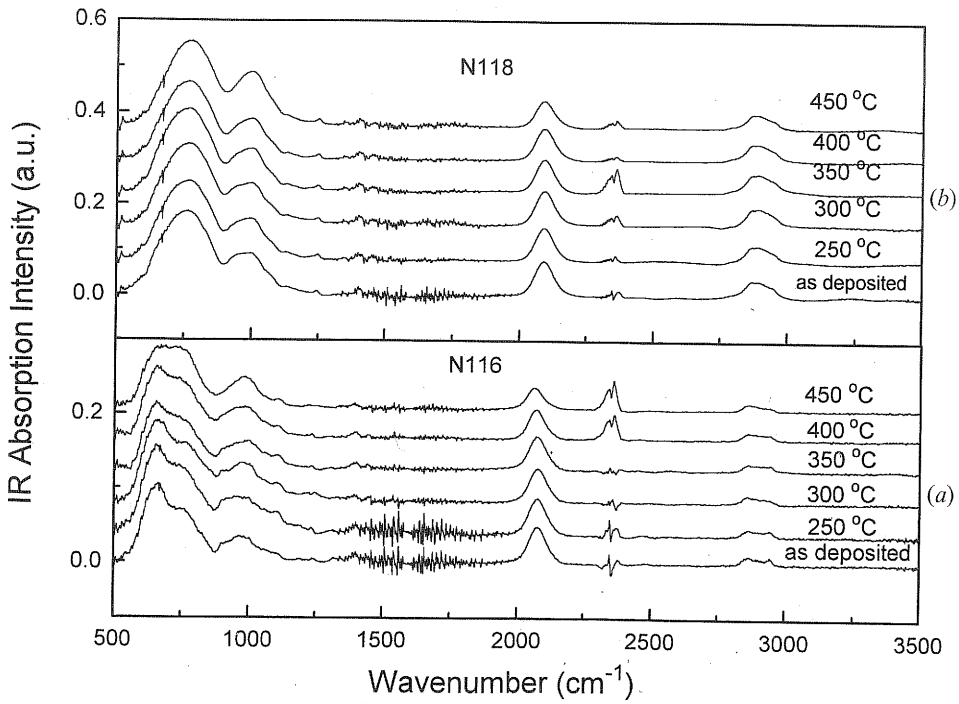
§ 3. Results

3.1. *Infrared spectroscopy*

We have reported the infrared spectra and their peak assignments for a-$Si_{1-x}C_x$: H films deposited by PECVD from different carbon sources (Demichelis *et al.* 1995a, b). To understand better the behaviours of the different bondings as functions of the annealing temperature for films with different carbon contents, we show the infrared spectra at different annealing temperatures in fig. 1. We focus our attention on three absorption regions:

(1) the modes at 630 cm^{-1} attributed to the Si–H wagging vibration, the modes at 670 cm^{-1} attributed to Si–C stretching vibration and the modes at 700–

Fig. 1



The infrared spectra of the samples at different annealing temperatures (a.u., arbitrary units): (*a*) sample N116; (*b*) sample N118.

800 cm^{-1} attributed to the $SiCH_3$ wagging vibrations (Weider, Cardona and Guarnieri 1979);

(2) the mode at 2100 cm^{-1} attributed to the stretching vibration of SiH_2 and C–SiH groups (Lucovsky 1979, Weider *et al.* 1979, Ouwens 1994);

(3) the region between 2800 and 3100 cm^{-1} assigned to stretching vibration of the CH_n groups (Dischler, Bubenzer and Koidl 1973, 1983).

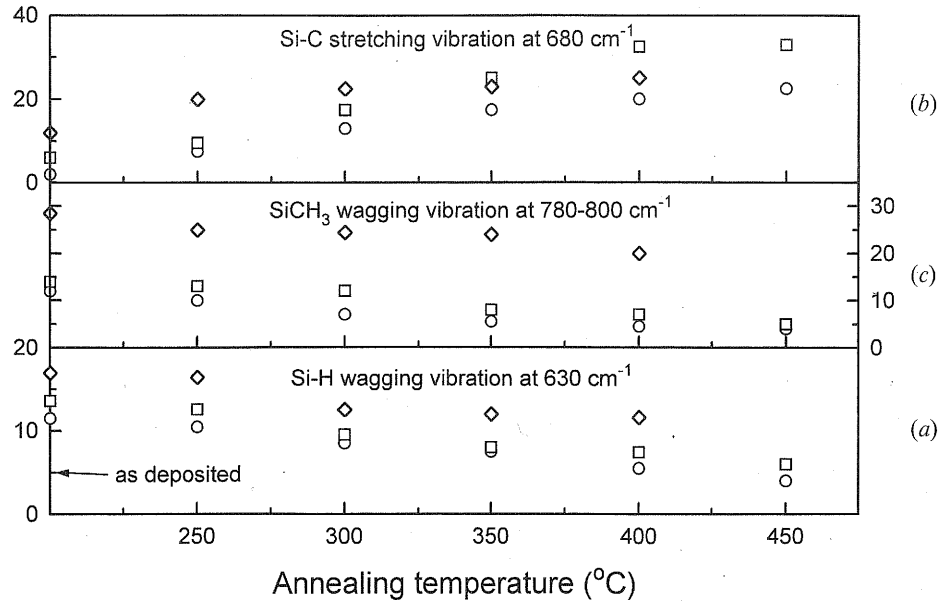
For comparison, we calculated the integrated intensities of the peaks defined as

$$\int \frac{\alpha(\omega)}{\omega} \, d\omega, \tag{1}$$

where α is the absorption coefficient, ω is the frequency in reciprocal centimetres and the integral is over the absorption band of interest.

Figure 2 (*a*) shows the integrated intensities of the Si–H wagging vibration at 630 cm^{-1} as a function of the annealing temperature. It can be seen that the infrared integrated intensities decrease with increase in annealing temperature. The trend of the integrated intensities of Si–C stretching mode at 670 cm^{-1} is given in fig. 2 (*b*). Its integrated intensities increase with increase in annealing temperature. Figure 2 (*c*) shows the integrated intensity of the peak at 780–800 cm^{-1} as a function of annealing temperature. This band is due to the rocking or wagging vibrations of the CH_3 radical attached to Si or Si–C. We can observe that its integrated intensity decreases with increase in annealing temperature, especially when the annealing temperature is

Fig. 2



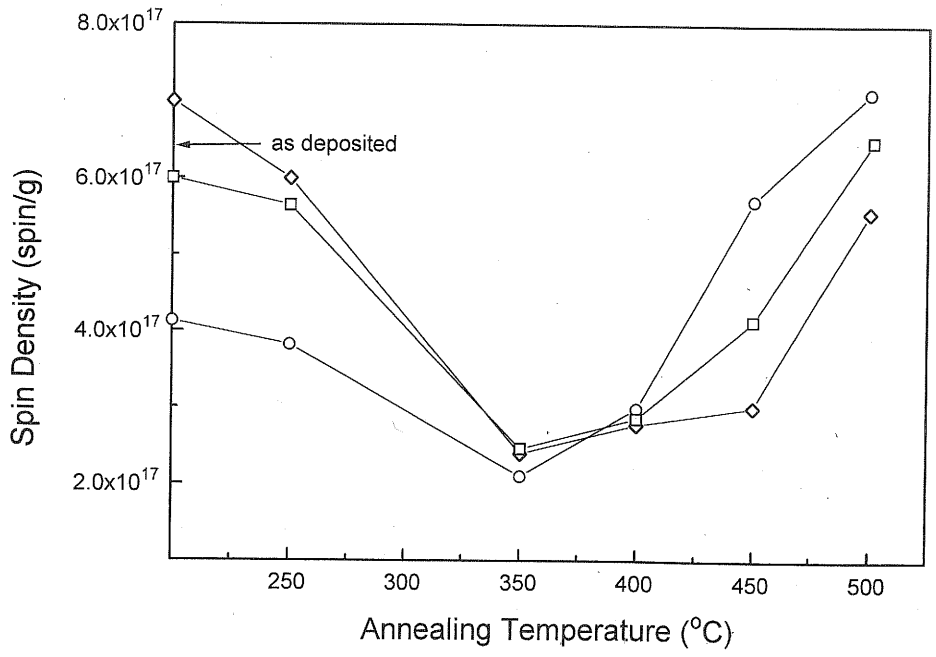
The infrared integrated intensities of the deconvoluted peaks as a function of annealing temperature for (*a*) the Si–H wagging vibration at 630 cm^{-1}, (*b*) the Si–C stretching vibration at 670 cm^{-1} and (*c*) the $SiCH_3$ rocking or wagging vibration at 780–800 cm^{-1}: (○), sample N116; (□), sample N92; (◇), sample N118.

over 350°C. A similar trend for a-$Si_{1-x}C_x$: H films with different carbon contents can be observed. The infrared peak at 2100 cm^{-1} can be deconvoluted into 2120 and 2065 cm^{-1} peaks. The peak at 2120 cm^{-1} was determined to be the vibration of the silicon atom bound with hydrogen atoms in a dihydride configuration and lying at internal surfaces of voids in films (Stein, Myers and Follstaedt 1993). Our experimental results indicate that the infrared peak at 2100 cm^{-1} shifts to 2080 cm^{-1} for annealing temperatures above 350°C. This result confirms the existence of hydrogen atoms in a dihydride configuration and demonstrates that those hydrogen atoms are unstable in high-temperature annealng. The band at 2800–3100 cm^{-1} is due to the convolution of the CH_n stretching vibration in the sp^3 and sp^2 configurations (Dischler *et al.* 1973, 1983). Our infrared results demonstrate that the integrated intensity of the infrared band at 2800–3100 cm^{-1} decreases with increase in annealing temperature. Thus the CH_2 and CH_3 groups in sp^3 configurations are unstable under high-temperature annealing.

3.2. *Electron spin resonance measurements*

In order to obtain additional information on the dependence of defect properties on the annealing temperature, an ESR measurement was performed on each sample with different annealing temperatures. For comparison, the values of the defect density N_s as a function of the annealing temperature are given in fig. 3. In order to explain our experimental results, the experimental temperature can be divided into two regions based on the results in fig. 3.

Fig. 3



The defect density N_s as a function of annealing temperature: (○), sample N116; (□), sample N92; (◇), sample N118.

3.2.1. *Low-temperature annealing (below 350°C)*

In the low-temperature range, the E_{04} and B values are approximately constant (see below). The density of dangling bonds decreases with increase in the annealing temperature and is a minimum at 350°C. At this temperature, the network undergoes relaxation and reconstruction; so a decrease in dangling bonds can be observed. In the a-$Si_{1-x}C_x$: H network, the formation of the voids is due to the existence of the SiH configuration. Carbon is incorporated into hydrogenated amorphous silicon (a-Si : H), which causes two side effects. One is new defects induced by carbon entering into the network, and the second is the formation of the SiHCH and CH_n configurations. The existence of new units is the main reason why there are more microvoids in a-$Si_{1-x}C_x$: H than in the a-Si : H. There are many dangling bonds in the internal surface of the voids. It can be observed that the defect density increases from $4{\cdot}13 \times 10^{17}$ to $7{\cdot}0 \times 10^{17}$ cm^{-3} for increase in the carbon content from 15 to 24 at.% (table). When a low-temperature annealing is carried out, weakly bound hydrogen is driven from the internal surface, which will cause 'collapse' of the voids, and so those dangling bonds having opposite spin states in the internal surface recombine to reduce defects (Trapeznikova, Kon'Kov, Terukov and Yastrebov 1994). On the other hand, with the release of hydrogen from the surface of the microvoids, followed by the trapping of the atoms on nearby dangling bonds, some of the dangling bonds are saturated by hydrogen. As a result, the density of dangling bonds decreases.

3.2.2. *High-temperature annealing (above 350°C)*

According to ESR data, the density of the dangling bonds increases in this temperature range. These results can be explained as follows. Above 350°C, a new stage of hydrogen effusion and structural rearrangement will occur. The strongly bound hydrogen in SiH, SiH_2, $(SiH_2)_n$, CH_n and $SiCH_3$ configurations escapes from the amorphous network. It is known that more hydrogen exists in the $(SiH_2)_n$ and CH_n configurations in a-$Si_{1-x}C_x$: H films from C_2H_2+SiH_4 than that in the a-$Si_{1-x}C_x$: H films from CH_4+SiH_4 with the same carbon content (Demichelis *et al.* 1995a,b). These hydrogen bonds in a polymeric phase are easily broken in a-$Si_{1-x}C_x$: H films from SiH_4+C_2H_2 above 350°C. However, a number of defects from hydrogen effusion are only observed in the a-$Si_{1-x}C_x$: H films from SiH_4+CH_4 when the annealing temperature is above 500°C (Trapeznikova *et al.* 1994). On the other hand, weak C–C, Si–Si and C–Si bonds will be broken in a-$Si_{1-x}C_x$: H films during high-temperature annealing, and many dangling bonds are formed. Although some dangling bonds can bridge over each other immediately or

Elemental compositions, Tauc gaps, E_{04} values, defect densities N_s and g values of a-$Si_{1-x}C_x$: H films deposited from C_2H_2+SiH_4 gas mixture against the gas rate ratios $[C_2H_2]/[C_2H_2+SiH_4]$.

Sample	$[C_2H_2]/[C_2H_2+SiH_4]$	$\frac{[C]}{[C+Si]}$	C (at.%)	Si (at.%)	H (at.%)	E_g (eV)	E_{04} (eV)	$N_s(\times 10^{17})$ (g^{-1})	g
N116	5	0·22	15	53·0	32·0	2·19	2·30	4·13	2·0053
N92	20	0·40	20·5	30·8	48·7	2·55	2·70	6·0	2·0050
N118	33	0·48	24·0	26·0	50	2·62	2·85	7·0	2·0043

after some structural rearrangement to reduce defects, such as Si–C bond formation, the process of defect production is stronger than that of defect annihilation. As a result, the defects increase with increase in the annealing temperature. This result can be further understood by infrared analysis. The integrated intensities of the Si–H wagging vibration at 630 cm^{-1}, the SiH_n stretching vibration at 2100 cm^{-1}, the $SiCH_3$ wagging vibration at 780–800 cm^{-1} and CH_n stretching vibration at 2800–3100 cm^{-1} decrease with increasing annealing temperature, which confirms hydrogen effusion and defect production. On the other hand, the integrated intensity of Si–C stretching vibration at 670 cm^{-1} increases with increasing annealing temperature, which indicates that annealing makes new Si–C networks form.

3.3. *The optical gap and E_{04} gap*

The optical Tauc gap E_g and absorption coefficients of the various samples were evaluated using standard techniques (Demichelis, Kaniadakis, Tagliaferro and Tresso 1987). E_g was determined by extrapolating the function

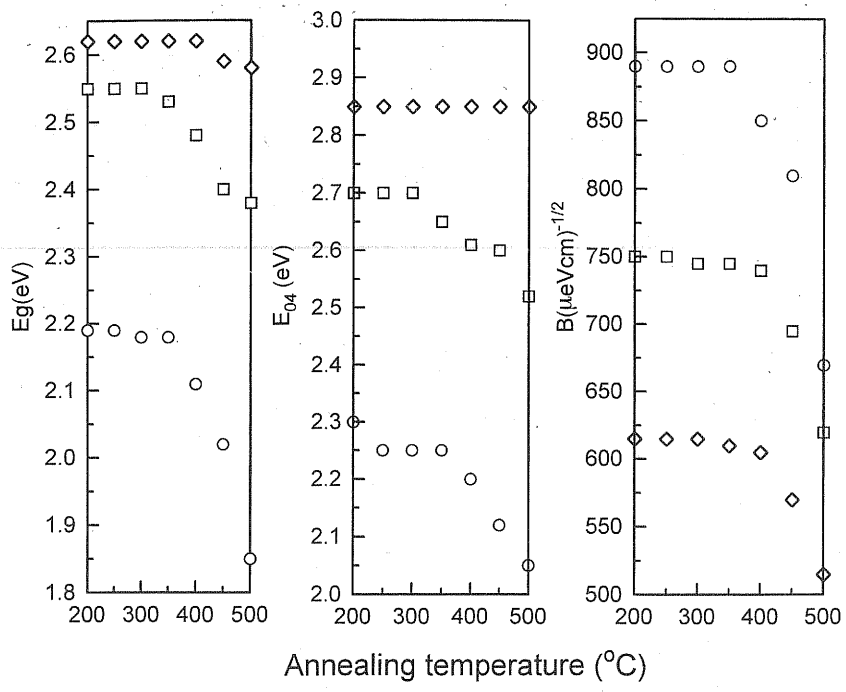
$$(\alpha E)^{1/2} = B(E - E_g) \tag{2}$$

to the horizontal axis, where α is the absorption coefficient and B is a proportionality constant (proportional to the optical joint density of states) (Tauc 1974). We chose a-$Si_{1-x}C_x$: H samples which change from silicon-like to carbon-rich with increase in carbon content from 15 to 24 at.%. The change is also confirmed by the abrupt reduction in the Tauc slope B from silicon-like values of $B = 890\,cm^{-1/2}\,eV^{-1/2}$ to carbon-rich values of $B = 615\,cm^{-1/2}\,eV^{-1/2}$ (Sotiropoulos and Weiser 1987). The E_g, E_{04} (the energy at which the absorption coefficients of $10^4\,cm^{-1}$) and B values as functions of annealing temperature are shown in fig. 4. It can be seen that the values are approximately constant for a-$Si_{1-x}C_x$: H films at low temperatures. They dramatically decrease for annealing temperatures over 350°C for silicon-like a-$Si_{1-x}C_x$: H films. The decrease in the B value with increase in the annealing temperature can be explained by some increase in the disorder of the structure (Mui, Basa and Smith 1986, Saito *et al.* 1985). It is clear from fig. 4 that the E_g, E_{04} and B values become stable with respect to annealing temperature with increasing carbon content. In other words, the themal stability of a-$Si_{1-x}C_x$: H film structure increases with increasing carbon content.

3.4. *Photoluminescence*

Figure 5 shows the PL spectra for a-$Si_{1-x}C_x$: H films with different carbon contents at different annealing temperatures. For low-carbon-content a-$Si_{1-x}C_x$: H film ($E_{04} < 2{\cdot}5$ eV), the PL signal increases at 250°C annealing; then the PL signal is quenched by the high-temperature annealing process (fig. 5 (*a*)). However, the PL signals are almost constant for different annealing temperatures for carbon-rich a-$Si_{1-x}C_x$: H films (fig. 5 (*b*)). In order to interpret our results, we discuss the electronic structure of inhomogeneous material. The infrared results indicate that a-$Si_{1-x}C_x$: H films are multiphase. Amorphous networks consist of SiH, SiC, $SiCH_3$ and CH_n units. Robertson (1992a) has calculated the densities of states of C–Si, C–SiC, CH and C in the sp^2 and sp^3 configurations. According to Brodsky's (1980) quantum well mode, we may divide them into two phases based on the theoretical results given by Robertson (1992a). One is the quantum well region composed of a-Si, a-$Si_{1-x}C_x$ or sp^2 C cluster (in the carbon-rich a-$Si_{1-x}C_x$: H films), and the other is the barrier

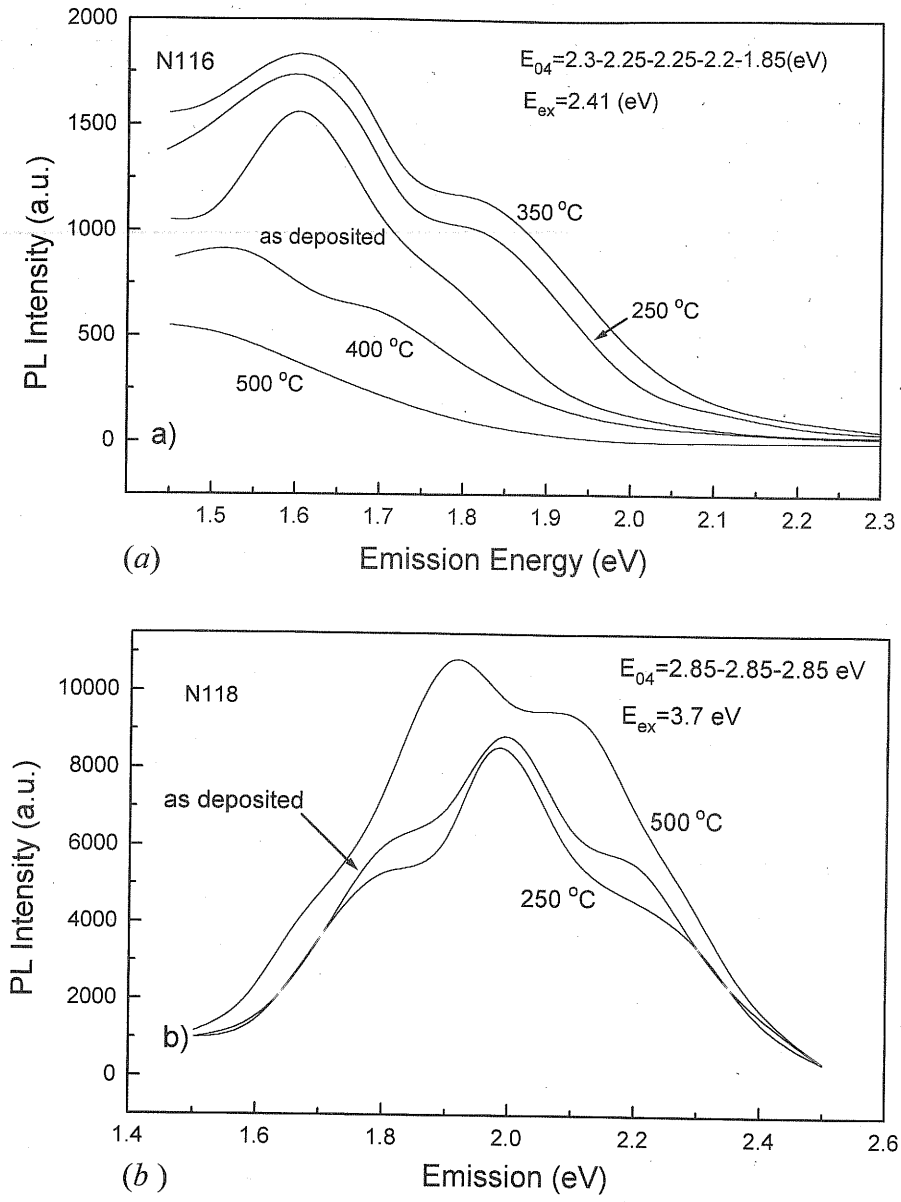
Fig. 4



The E_g, E_{04} and B values as a function of annealing temperature: (○), sample N116; (□), sample N92; (◇), sample N118.

region composed of CH, SiH, SiHCH and C at sp^3 sites (in carbon-rich a-$Si_{1-x}C_x$: H films). As carbon atoms enter the a-Si : H network, the SiC, CH and SiCH phases will increase. Owing to a quantum well effect, the larger barrier height of CH_n and SiHCH phase results in a higher ground-state energy for electrons in the well compared with SiH_n in the a-Si : H network. Our results show blue shifts of the PL peak with increase in carbon content (Demichelis *et al.* 1995a). This blue shift is due to the increase in the density and the size of the CH_n and SiHCH units, so that the ground state in the well is pushed upwards. As the material is annealed above 350°C, a red shift of the PL peak is observed for silicon-like a-$Si_{1-x}C_x$: 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. These observations are similar to those reported in the literature (Sab, Tsai and Lee 1989). This is due to hydrogen effusion, resulting in a decrease in the content of CH_n and SiHCH, so that the confining action of barrier becomes weak. Thus the ground-state energy of electron in the wells will decrease. When a low-temperature anneal is applied to a silicon-rich a-$Si_{1-x}C_x$: H film, a structural rearrangement process occurs (see ESR results), and the defect density decreases. In the silicon-like a-$Si_{1-x}C_x$: H material, these defects are correlated with non-radiative recombination centres (Street 1978, Stutzmann 1989). So it can be observed that the PL intensity increases with increase in annealing temperature. At annealing temperatures above 350°C, defects increase because of hydrogen effusion, which will lead to increasing non-radiative recombination centres, resulting in PL signal quenching. Moreover, in the silicon-like a-

Fig. 5



The PL spectra for a-$Si_{1-x}C_x$: H films with different carbon contents at different annealing temperatures (a.u., arbitrary units): (*a*) sample N116; (*b*) sample N118.

$Si_{1-x}C_x$: H film, according to the weak-bond-to-dangling-bond conversion model (Stutzmann 1989) under non-equilibrium excitation conditions, such as illumination by intense light, excess charge carriers may be trapped in the weak-bond states deepest in the pseudo-gap and cause them to dissociate, leading to the formation of metastable dangling-bond defects, which is another reason for the reduced PL intensity.

3.5. *Photoluminescence spectra for carbon-rich hydrogenated amorphous silicon–carbon alloy films*

For increasing annealing temperature, the PL intensity is almost constant for carbon-rich a-$Si_{1-x}C_x$: H films, which is completely different PL behaviour from the silicon-like a-$Si_{1-x}C_x$: H films. These results can be explained as follows. For carbon-rich a-$Si_{1-x}C_x$: H films, with increasing annealing temperature, the concentration of the CH_n, SiHCH and SiH units will decrease; so the confining action of the barrier region becomes weaker. Moreover, the defect density increases with increasing annealing temperature, and these seem to decrease the PL signals. However, almost constant PL intensity is experimentally observed, which indicates that the annealing process does not seriously affect PL signals. In carbon-rich a-$Si_{1-x}C_x$: H films, the presence of clustering has a pronounced effect on the luminescence properties (Robertson 1992a,b). As the carbon content rises, the formation of π-bond clusters in local environments may be anticipated. In π-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 final states because they tend to be localized in different regions of real space. In π-bonded clusters, valence- and conduction-band states are localized in the same part of real space (Robertson 1992a). These states then have a significant overlap, and L–L transitions are allowed. As π-bonded clusters form in carbon-rich a-$Si_{1-x}C_x$: H, the overlap probability of L–L states increases with increase in π-bonded clusters. This may account for the difference between the PL behaviours of silicon-like and carbon-rich a-$Si_{1-x}C_x$: H alloys. In a-Si : H and silicon-like a-$Si_{1-x}C_x$: H, the silicon dangling bonds are the main non-radiative recombination channel, which causes strong correlation between the PL signal and the defect density, and it can be observed that the PL intensity decreases with the increase in defects. In carbon-rich a-$Si_{1-x}C_x$: H alloys, we find little correlation between luminescence and defect density, even though the defect density changes in the annealing process, which suggests that recombination is not particularly associated with defects. Liedtke, Jahn, Finger and Fuhs (1987) and Liedtke *et al.* (1989) reported the weak dependence of PL efficiency on defect density in carbon-rich materials. This supports our results. The near independence of PL intensity on defects for carbon-rich a-$Si_{1-x}C_x$: H films (fig. 5(*b*)) suggests that luminescence is associated with clusters in an intracluster process (Robertson 1992a).

§ 4. Conclusions

From the various experimental results, we characterized the thermal stability of a-$Si_{1-x}C_x$: H films. By analysis and discussion, we can obtain some important results as follows.

The Si-H wagging vibrations at 630 cm^{-1} and stretching vibration at 2100 cm^{-1}, the Si–CH_3 rocking or wagging vibrations at 780–800 cm^{-1} and the CH_n stretching vibrations at 2800–3100 cm^{-1} in the sp^3 and sp^2 configurations all decrease with increase in annealing temperature. The Si–C stretching vibration at 680 cm^{-1} increases. The modification of the bonding configuration with respect to annealing temperature was characterized. We confirm the existence of hydrogen atoms in a dihydride configuration that is unstable for high-temperature annealing. For low-temperature annealing, the network undergoes relaxation and reconstruction, and dangling bonds are saturated by hydrogen, which results in a decrease in dangling bonds with increasing annealing temperature. For high annealing temperatures,

weak C–C, Si–Si and C–Si bonds will be broken, and a new stage of hydrogen effusion and structural rearrangement will occur. The strongly bound hydrogen in the SiH_n, $(SiH_2)_n$, CH_n and $SiCH_3$ configurations escapes from the amorphous network, which causes an increase in defects. The dependence of the E_g, E_{04} and B values on annealing temperature reveals that the thermal stability of the a-$Si_{1-x}C_x$: H film structure increases with carbon content. In silicon-like a-$Si_{1-x}C_x$: H alloys, the silicon-dangling bonds are the main non-radiative recombination channel, which causes a strong correlation between the PL signal and defect density. The red shift of the PL peak is correlated with the destruction of the confining power of barriers. In carbon-rich a-$Si_{1-x}C_x$: H alloys, π-bonded clusters play an important role in the luminescence process. The recombination of the band tail to band tail (L–L) is the main process. The PL intensity has little dependence on the defect density in carbon-rich a-$Si_{1-x}C_x$: H owing to an intracluster process. So the thermal stability of the luminescence increases in carbon-rich a-$Si_{1-x}C_x$: H films.

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References

Akita, S., Nakayama, Y., Yamano, M., and Kawamura, R., 1989a, Amorphous Silicon Technology, Materials Research Society Symposium Proceedings, Vol. 149, edited by A. Madan, E. A. Schiff, M. J. Thompson, K. Tanaka and P. G. LeComber (Pittsburgh, Pennsylvania: Materials Research Society), p. 167.

Akita, S., Wakita, K., Nakayama, Y., and Kawamura, T., 1989b, *Amorphous and Crystalline Silicon Carbide*, Springer Proceeding in Physics, Vol. 34, edited by G. L. Harris and C. Y. W. Yang (Berlin: Springer), p. 77.

Brodsky, M. H., 1980, *Solid St. Commun.*, **36**, 55.

Chang, K. C., Chang, K. Y., Fang, J. K., and Jwo, S. C., 1987, *IEEE Electron Devices Lett.*, **8**, 64.

Demichelis, F., Crovini, G., Giorgis, F., Pirri, C. F., and Tresso, E., 1995a, *Diamond Related Mater.* **4**, 127.

Demichelis, F., Crovini, G., Pirri, C. F., Tresso, E., Galloni, R., Rizzoli, R., Summonte, C., Zignani, F., Rava, P., and Madan, A., 1994, *Phil. Mag.* B, **69**, 377.

Demichelis, F., Giorgis, F., Pirri, C. F., and Tresso, E., 1995b, *Phil. Mag.* A, **72**, 913.

Demichelis, F., Kaniadakis, G., Tagliaferro, A., and Tresso, E., 1987, *Appl. Optics*, **26**, 1737.

Demichelis, F., Pirri, C. F., Tresso, E., Adriaenssens, G. J., Grevendonk, W., Herremans, H., Amato, G., and Coscia, U., 1993, *Appl. Surf. Sci.*, **70–71**, 664.

Dischler, B., Bubenzer, A., and Koidl, P., 1973, *J. appl. Phys.*, **42**, 636; 1983, *Solid St. Commun.*, **48**, 105.

Liedtke, S., Jahn, K., Finger, F., and Fuhs, W., 1987, *J. non-crystalline Solids*, **97**, 1083.

Liedtke, S., Lips, K., Bort, M., Jahn, K., Finger, F., and Fuhs, W., 1989, *J. non-crystalline Solids*, **114**, 516.

Lin, S., and Feldman, B., 1983, *Phil. Mag.* B, **47**, 113.

Lucovsky, G., 1979, *Solid. St. Commun.*, **29**, 571.

Matsuda, A., Yamaoka, T., Wolff, S., Koyama, Y., Himanishi, Y., Kamoka, H., Matsuura, H., and Tanaka, K., 1980, *J. appl. Phys.*, **60**, 4025.

Mui, K., Basa, D. K., and Smith, F. W., 1986, *J. appl. Phys.*, **59**, 582.

Ouwens, J. D., Schropp, R. E. I., and van der Weg, W. F., 1994, *Appl. Phys. Lett.*, **65**, 204.

Roberston, J., 1992a, *Phil. Mag.* B, **66**, 615, 1992b, Ibid., **66**, 199.

Sab, W. J., Tsai, H. K., and Lee, S. C., 1989, *Appl. Phys. Lett.*, **54**, 617.

SAITO, N., YAMADA, T., YAMAGUCHI, T., NAKAAKI, I., and TANAKA, N., 1985, *Phil. Mag.* B, **52**, 987.
SOLOMON, I., SCHMIDT, M. P., and TRAN-QUOC, H., 1988a, *Phys. Rev.* B, **38**, 9895.
SOLOMON, I., SCHMIDT, M. P., SENEMAUD, C., and KHODJA, D. M., 1988b, *Phys. Rev.* B, **38**, 13 263.
SOTIROPOULOS, J., and WEISER, G., 1987, *J. non-crystalline Solids*, **92**, 95.
STEIN, H. I., MYERS, S. M., and FOLLSTAEDT, D. M., 1993, *J. appl. Phys.*, **73**, 2755.
STREET, R. A., 1978, *Phil. Mag.* B, **37**, 35.
STUTZMANN, M., 1989, *Phil. Mag.* B, **60**, 531.
TAUC, J., 1974, *Amorphous and Liquid Semiconductors*. (London: Plenum).
TAWADA, Y., KONDO, K., OKAMOTO, H., and HAMAKAWA, Y., 1982, *J. appl. Phys.*, **53**, 5273.
TRAPEZNIKOVA, I. N., KON'KOV, O. I., TERUKOV, E. I., and YASTREBOV, S. G., 1994, *Phys. Solid State*, **36**, 1519.
WEIDER, H., CARDONA, M., and GUARNIERI, C. R., 1979, *Phys. Stat. sol.* (b), **92**, 99.