JOURNAL OF MATERIALS SCIENCE 24 (1989) 3096–3100

Microstructural changes of Al/amorphous SiC layered films subjected to heating

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Layered specimens composed of aluminium and a-SiC films were prepared at room temperature by r.f. magnetron sputtering. a-SiC/Al/a-SiC triple-layered films were heated in the transmission electron microscope (TEM), and the *in-situ* microstructural changes were observed continuously. In order to estimate the interfacial reaction process kinematically, electrical resistance measurements were conducted on Al/a-SiC double-layered films heated isothermally at 573, 598 and 623 K. The *in-situ* TEM observations showed that no pronounced interfacial reactions occurred up to about 600 K, that silicon precipitates were formed and grew around 673 K, and that Al_4C_3 compounds were produced during heating at temperatures above about 753 K. The electrical resistance of Al/a-SiC double-layered film heated isothermally increased gradually with heating time, and this increase was closely related to the volume fraction of silicon precipitates in the aluminium film. From the kinematical analyses of the results of electrical resistance measurements, an activation energy of the interfacial reaction process of aluminium with a-SiC films in the temperature range 573 to 623 K was found to be about 2.6 eV, being close to the bond energy of Si–C.

1. Introduction

In recent years a large number of investigations has been carried out on opto-electronic properties of tetrahedrally bonded amorphous semiconductor films and hydrogenated ones, such as amorphous silicon (a-Si, a-Si:H) and amorphous silicon carbide (a-SiC, a-SiC:H) films [1–5]. In these materials, a-SiC and a-SiC:H films have attracted much attention as potential materials for solar cell production [6, 7], because of their efficient opto-electronic properties and their heat, wear and corrosion resistant properties. In such a microelectronics industry, aluminium thin films are used widely as an electrode material. However, the interfacial microstructures of amorphous semiconductor films in contact with aluminium electrode films with and without heating have been studied very little [8–10], in spite of the fact that they are considered to affect the fundamental properties of the amorphous films greatly: they are not only important in interpreting the results of electrical measurements made on metal-contacted amorphous semiconductor films, as pointed out by Mei *et al.* [11], but they also influence the service lifetime of devices.

The purpose of the present work was to investigate the microstructural changes in the layered specimens composed of aluminium and a-SiC films subjected to heating in a transmission electron microscope, and to discuss the interfacial reaction processes of aluminium with a-SiC films by means of the electrical resistance measurements.

2. Experimental procedure

Double-layered and triple-layered specimens composed of a-SiC and aluminium films, each 150 nm thick, were prepared without breaking the vacuum using an r.f. planar magnetron sputtering apparatus with two kinds of target, aluminium and sintered SiC discs. These targets were sputtered alternately at a power of 270 W in pure argon gas at a pressure of 0.65 Pa, where the background pressure before sputtering was 3.6×10^{-5} Pa. For the preparation of the triple-layered specimen, a-SiC film was first sputter-deposited on an (0 0 1) Si wafer, then aluminium film was deposited on the initial a-SiC film and lastly, a-SiC film on the aluminium film (a-SiC/Al/a-SiC). For the double-layered film, a-SiC film and then aluminium film were deposited on the glass substrate (Al/a-SiC). The substrate temperature was room temperature. Under these conditions, the deposition rates of a-SiC and aluminium films obtained were 25 and 100 nm min^{-1}, respectively.

Transmission electron microscope (TEM) specimens of a-SiC/Al/a-SiC triple-layered films were made by chemical etching of the silicon substrates. Such a TEM specimen was heated in the temperature range 300 to 873 K within the TEM, and the *in situ* change of the microstructure during the heating process was observed continuously. The TEM employed was HU-3000 operating at 2000 keV.

The double-layered films on the glass substrates were used for the kinematical study of the interfacial

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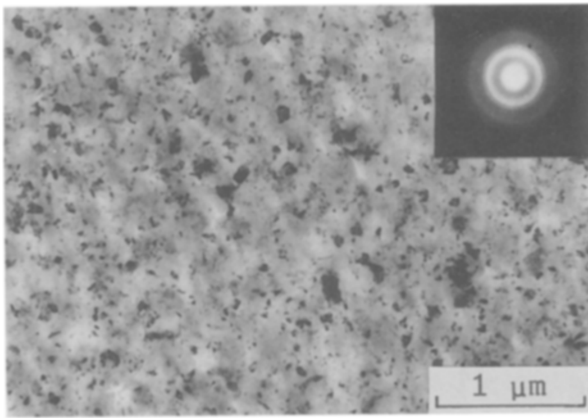

Figure 1 Transmission electron micrograph of a-SiC/Al/a-SiC triple-layered film.

reaction of aluminium film in contact with a-SiC film when they were subjected to heating. The samples of dimensions approximately $15 \times 30\,mm^2$ were heated isothermally at 573, 598 and 623 K in a quartz tube furnace with a flow of argon gas. The changes in the electrical resistance of aluminium film with heating times were measured by the four-point probe method, using a Keithley 503 Milliohmmeter. Furthermore, the surface and the interface of the heated specimens were observed by optical microscopy, where the interface was revealed by dissolving the aluminium layer with 10% HF solution. As a comparison, the electrical resistance measurements and the optical microscopic observations were carried out on Al/a-Si double-layered films, which were prepared under the same conditions as those for Al/a-SiC layered specimens but using the silicon wafer target instead of the SiC disc.

3. Results and discussion

3.1. *In situ* observations of layered specimens heated within the TEM

The microstructure and the continuity of the films prepared by sputtering on silicon substrates at room temperature were examined with TEM. TEM observations revealed that SiC films having a thickness of more than 50 nm and aluminium films of more than 30 nm were continuous without channels and holes, and that they were amorphous and polycrystalline structures, respectively. Fig. 1 shows a transmission electron micrograph of a-SiC/Al/a-SiC triple-layered film with each layer 150 nm thick. The diffraction pattern is composed of polycrystalline rings from the aluminium layer and an amorphous halo pattern from the a-SiC layers. The TEM image shows that aluminium grains are present in the bright and grey contrasts. Such a contrast indicates non-uniformity of the thickness of a-SiC film on the aluminium film, which resulted from the shadowing effects [12] during preparation of a-SiC on aluminium due to aluminium surface irregularities such as hillocks [13].

The triple-layered films were heated in the range 300 to 873 K, and the microstructural changes were observed continuously. Fig. 2 shows typical results, in which (a) to (e) are the TEM images and the selected-area diffraction patterns at various temperatures which correspond to the points indicated in the heating process (f), respectively. There was no visible change in the microstructure with increasing temperature up to about 600 K. However, in the vicinity of 673 K, many precipitates appeared suddenly and grew, as shown by an arrow in Fig. 2a, and the selected-area diffraction patterns of such precipitates contained some diffraction spots in the halo pattern, as seen in Fig. 2a. From analyses of the diffraction spots, the precipitates were identified as crystalline silicon. Fig. 2b was taken after the specimen was kept at 673 K for 10 min. By comparing (a) to (b) it is noted that silicon crystallites did not grow on further heating at 673 K. When the temperature was increased to 753 K, a drastic change in the structure occurred as seen in Fig. 2c: the contrast between the aluminium grains and silicon crystallites disappeared, and the diffraction pattern changed into the halo pattern without aluminium polycrystalline rings. When the sample

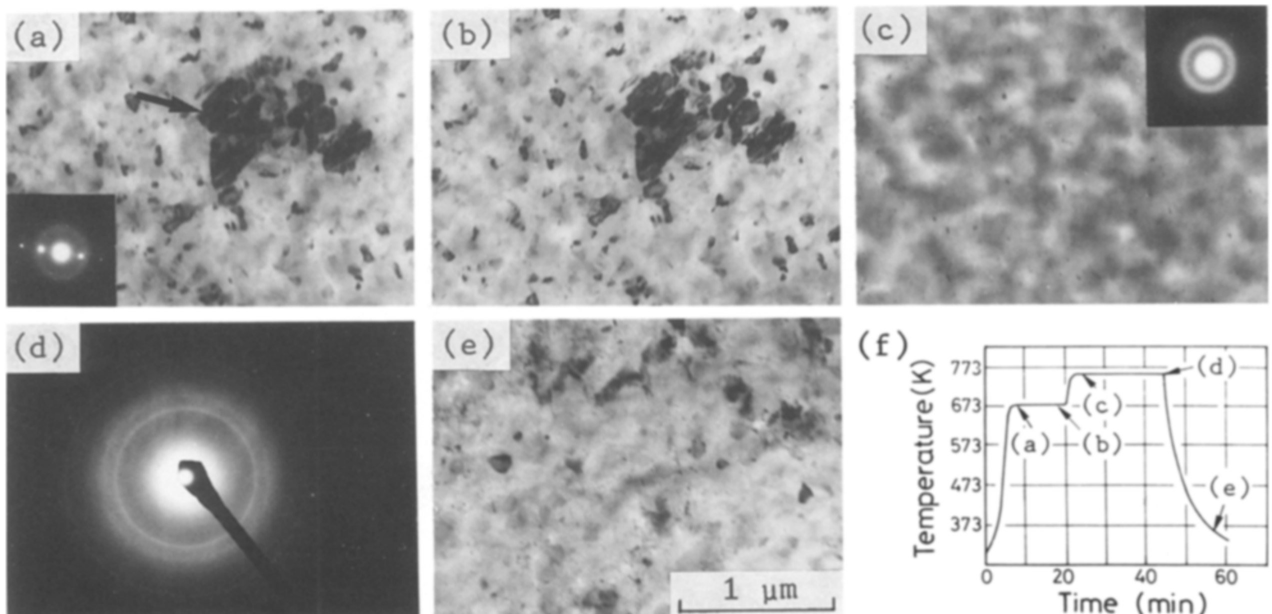

Figure 2 Microstructural changes of a-SiC/Al/a-SiC triple-layered film during *in situ* heating in the TEM. (a) to (e) correspond to the points in heating cycle (f).

was heated at 753 K for 15 min, diffraction rings were observed in the halo pattern, as represented in Fig. 2d. Analyses of the rings showed that they were from Al_4C_3 compounds, although the contrast between these reaction products was not present with the TEM mode. On decreasing the temperature, the contrast between the aluminium grains and silicon precipitates began to appear again, as seen in Fig. 2e, showing the structure after cooling down to about 373 K.

The crystallization temperatures of a-Si and a-Ge films have been reported to be greatly reduced due to the presence of metal films on these amorphous films [8, 14]. The crystallization of a-SiC film occurred when it was heated above 1273 K [15]. During the *in situ* TEM observations for a-SiC/Al/a-SiC layered films heated below 873 K, crystallization of a-SiC films did not seem to occur.

3.2. Electrical resistance measurements

It was confirmed from the *in situ* TEM observations that no pronounced interfacial reactions were visible up to about 600 K, that silicon precipitates were formed suddenly and grew around 673 K, and that Al_4C_3 compounds were produced during heating at temperatures above 753 K. In order to obtain the information on the behaviour of silicon and carbon atoms, electrical resistance measurements were conducted on Al/a-SiC double-layered films heated isothermally at 573, 598 and 623 K. These temperatures were selected, because the interfacial reactions appeared to be very gradual, judging from the *in situ* TEM observations. As a comparison, resistance measurements were also carried out on Al/a-Si double-layered films. The typical resistance–time curves of Al/a-SiC and Al/a-Si double-layered films heated at 573 and 623 K, respectively, are shown in Fig. 3. It was found that the resistance increased gradually after the incubation period, and finally reached a constant value after longer heating periods. A similar behaviour was observed in the specimens heated at other temperatures. It was also noted that the period required for attaining the constant resistance value depended on the heating temperature: the higher the temperature the shorter the period required.

The surface and interface of the specimens after prolonged heating were observed by the optical microscopy. Fig. 4 shows the optical micrographs for the Al/a-SiC specimen heated at 573 K for 20 h. In Fig. 4a, the surface has irregularly shaped precipitates in the aluminium matrix. They corresponded to silicon crystallites, as observed previously by TEM. In Fig. 4b,

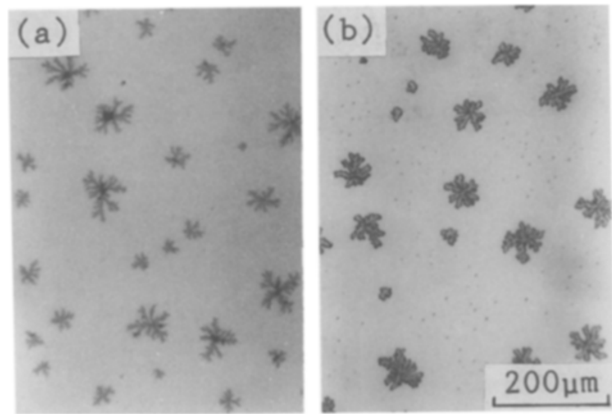

Figure 4 Optical micrographs of (a) surface and (b) interface of Al/a-SiC double-layered film heated at 573 K for 20 h.

the interface was revealed by dissolving only the aluminium film with HF solution, so that only silicon precipitates remain on the smooth interface. Similar precipitates were also observed for the heated Al/a-SiC double-layered films.

From such optical observations, the measured electrical resistance was interpreted to give a simple linear relationship with the volume fraction of crystalline silicon in the aluminium layer. Thus, the fraction of silicon precipitates in the aluminium film, $X(t)$, after a heating time t, can be given as

$$X = [\varrho(t) - \varrho(0)]/[\varrho(\infty) - \varrho(0)] \quad (1)$$

where $\varrho(t)$ is the electrical resistance at time t, and $\varrho(0)$ and $\varrho(\infty)$ are the initial and the final resistances, respectively. The calculated values of $X(t)$ for Al/a-SiC double-layered films heated at 573, 598 and 623 K are shown in Fig. 5. Each curve is seen to have a sigmoidal shape. The sigmoidal reaction curves can be analysed in terms of the Johnson–Mehl equation [16]

$$X(t) = 1 - \exp[-(Kt)^n] \quad (2)$$

where K is the rate constant and n is the growth exponent. By rewriting Equation 2

$$\log[\log 1/1 - X(t)] = n \log t + n \log K + \log e \quad (3)$$

Fig. 6 shows plot of $\log[\log 1/1 - X(t)]$ against $\log t$ for each isothermal heating of Al/a-SiC layered films, in which the straight lines are seen. The value of K at each heating temperature was obtained from the intercept of a straight line with the ordinate axis, as recognized from Equation 3. If the interfacial reaction process follows a thermal activation process, the value

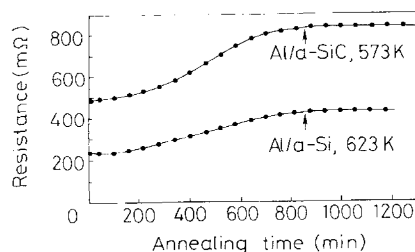

Figure 3 Electrical resistances plotted against heating times of Al/a-SiC and Al/a-Si double layered films heated at 573 and 627 K, respectively.

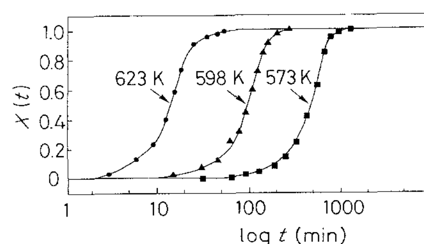

Figure 5 $X(t)$ plotted against duration, t, of the isothermal heating for Al/a-SiC double-layered films.

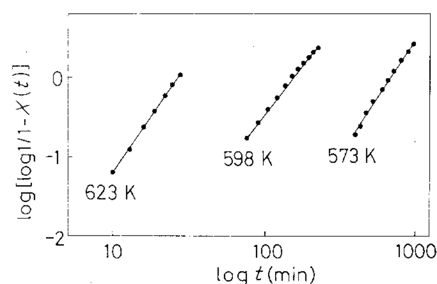

Figure 6 Plot of log [log 1/1 − $X(t)$] against log t.

of K in Equation 3 is given by an equation of the Arrhenius form

$$K = K_0 \exp(-E/kT) \quad (4)$$

where K_0 is a constant, k Boltzmann constant, T the absolute temperature, and E the activation energy. Plots of log K against $1/T$ for Al/a-SiC double-layered films are shown by the solid circles in Fig. 7. The open circles in Fig. 7 are the results for Al/a-Si double-layered films which were obtained in the same manner as Al/a-SiC double-layered films mentioned above. The experimental plots are on the straight lines whose slopes correspond to the overall activation energies of E = 2.6 and 1.3 eV for Al/a-SiC and Al/a-Si double-layered films, respectively.

3.3. Interfacical reaction processes

From the *in situ* TEM and the optical microscopic observations, it seems reasonable to consider that the behaviour of a-SiC film in contact with aluminium film subjected to heating may involve many reaction processes; the separation of Si–C bonds, the diffusion of silicon and carbon atoms through aluminium film, the precipitation and growth of crystalline silicon, and the formation of Al_4C_3 compounds.

According to the phase diagram of Al–C [17], the solubility of carbon in molten aluminium is very small; it is estimated below 0.05 wt % at 1573 to 1773 K, but there is a great tendency to form Al_4C_3. Bermudez [18] studied the interfacial reactions between the aluminium film having a thickness of less than two monolayers and SiC single crystal as a function of annealing temperature, using Auger and electron energy-loss spectroscopies. His results showed that annealing at the temperatures below 873 K caused aggregations of aluminium at carbon-rich sites, and that aluminium reacted with carbon to form Al_4C_3 compounds at the higher temperature. Iseki *et al.* [19], who investigated the interfacial reactions between sintered SiC and liquid aluminium, reported that Al_4C_3 phase was formed at the interface by the following

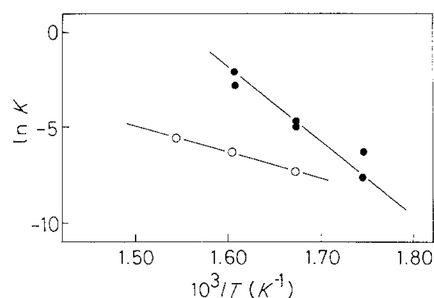

Figure 7 The inverse temperature dependence of rate constant K, for (○) Al/a-Si, E = 1.3 eV, and (●) Al/a-SiC, E = 2.6 eV.

reaction of

$$3SiC(s) + 4Al(l) = Al_4C_3(s) + 3Si(s) \quad (5)$$

where s and l are solid and liquid phases, respectively. They also found from the thermodynamical point of view that this reaction proceeded only by addition of silicon into liquid aluminium. Judging from their report, the drastic changes in the microstructure as seen in Figs 2c and d may suggest that aluminium film became a liquid-like phase, and that silicon atoms diffused into such an aluminium phase and Al_4C_3 compounds were formed by Reaction 5.

From the facts described above, it can be considered that the diffusivity of carbon atoms into the solid aluminium at the higher temperature and even into the molten aluminium is very small, and so that Al_4C_3 compounds may be made only in the neighbourhood of the interface while Al/a-SiC double-layered films were heated above 753 K. Thus, in the temperature range 573 to 623 K, in which the electrical resistance measurements were conducted, it can be considered that the interfacial reactions of Al/a-SiC layered films may not involve the processes of carbon diffusion and of Al_4C_3 formation. The activation energy derived for Al/a-SiC double-layered films over such a temperature range can be recognized to be caused by the release of silicon and carbon, silicon diffusion, and/or silicon precipitation. Table I summarizes the activation energies for Al/a-SiC and Al/a-Si double-layered films obtained in the present work, and the bond energies of Si–C and Si–Si. Also the activation energies for the diffusion and precipitation of silicon in aluminium are given in Table I, as given by the researchers who studied the interactions of aluminium film with silicon bulk crystal [20] and with crystalline silicon film [21]. These reported values are slightly smaller than the energy measured for Al/a-Si and much smaller than that for Al/a-SiC. This may suggest that the processes of diffusion and precipitation of silicon play a minor role in the interfacial reaction between aluminium and a-SiC films. On the other hand, the activation energies

TABLE I Activation and bond energies

	Activation energy (eV)	Bond energy (eV)
Interfacial reaction of Al/a-SiC	2.6	
Interfacial reaction of Al/a-Si	1.3	
Diffusion and precipitation of Si in Al [20, 22]	0.8–0.9	
Si–C		3.0
Si–Si		1.8

for Al/a-SiC and Al/a-Si films measured in this work are close to the bond energies of Si–C and Si–Si, respectively, although they are somewhat smaller. Assuming that the processes of the release of silicon and carbon, silicon diffusion and silicon precipitation take place in series, it can be mentioned that the release of silicon and carbon play a major role in the interfacial reaction between aluminium and a-SiC films heated in the temperature range 573 to 623 K.

In order to obtain more details of the interfacial reaction, the microscopic mechanisms for the diffusion of silicon, and the precipitation and growth of crystalline silicon ought to be clarified.

4. Conclusions

a-SiC/Al/a-SiC triple-layered films prepared at room temperature by r.f. magnetron sputtering were heated within the TEM, and the *in situ* change of the structure was observed continuously. Also the electrical resistance measurements were carried out on Al/a-SiC double-layered films. The results obtained are as follows.

1. The *in situ* TEM observations revealed that no pronounced interfacial reactions occurred up to about 600 K, that silicon precipitates were formed and grew around 673 K, and that Al_4C_3 compounds were produced during heating at temperatures above about 753 K. It was found from these observations that the possible interfacial reactions of a-SiC with aluminium films consisted of the separation of Si–C bonds, the diffusion of these atoms, the precipitation and growth of crystalline silicon, and the formation of Al_4C_3 compounds.

2. The electrical resistances of Al/a-SiC double-layered films heated isothermally at 573, 598 and 623 K increased gradually after some incubation periods and finally reached a constant value after the longer heating periods. The optical microscope observations of the heated specimens showed that such a behaviour of resistance was closely related to the volume fraction of silicon precipitates in the aluminium film.

3. From the kinematical analyses of the results of electrical resistance measurements, an activation energy of the interfacial reaction process of aluminium with a-SiC films in the temperature range 573 to 623 K was found to be about 2.6 eV, and this value is close to the bond energy of Si–C. This may suggest that the process of separation of silicon and carbon plays a major role in the interfacial reaction between aluminium and a-SiC films heated over the temperature range 573 to 623 K.

Acknowledgements

The authors thank Professor H. Fujita for his continuous encouragement and Messrs K. Yoshida, M. Komatsu and T. Sakata, Research Centre for Ultra-High Voltage Electron Microscopy, Osaka University, for their kind cooperation with high voltage electron microscope. They thank Mr Y. Okuyama for his help in the present research.

References

1. H. WIEDER, M. CARDONA and C. R. GUARUIERI, *Phys. Status Solidi (b)* **92** (1979) 99.
2. R. S. SUSSMAN and R. OGDEN, *Phil. Mag. (b)* **44** (1981) 137.
3. J. SARIE, T. FUJII, M. YOSHIMOTO, K. YAMAZOE and H. MATSUNAMI, *Thin Solid Films* **117** (1984) 59.
4. N. SAITO, *J. Appl. Phys.* **58** (1985) 3504.
5. K. MUI, D. K. BASA and F. W. SMITH, *ibid.* **59** (1986) 582.
6. D. A. ANDERSON and W. E. SPEAR, *Phil. Mag.* **35** (1977) 1.
7. Y. TAWADA, M. KONDO, H. OKAMOTO and Y. HAMAKAWA, *Solar Energy Mater.* **6** (1982) 237.
8. J. E. GREENE and L. MEI, *Thin Solid Films* **37** (1976) 429.
9. G. OTTAVIANI, D. SIGURD, V. MARRELLO, J. W. MAYER and J. O. McCALDIN, *J. Appl. Phys.* **45** (1974) 1730.
10. S. ISHIHARA, T. HIRAO, K. MORI, M. KITAGAWA, M. OHNO and S. KOHIKI, *ibid.* **53** (1982) 3909.
11. L. MEI and J. E. GREENE, *J. Vac. Sci. Technol.* **11** (1974) 145.
12. J. A. THORNTON, *Ann. Rev. Mater. Sci.* **7** (1977) 239.
13. D. S. HERMAN, M. A. SCHUSTER and R. M. GERBER, *J. Vac. Sci. Technol.* **9** (1979) 515.
14. S. R. HERD, P. CHAUDHARI and M. H. BRODSKY, *J. Non-Cryst. Solids* **7** (1972) 309.
15. S. INOUE, K. YOSHII, M. UMENO and H. KAWABE, *Thin Solid Films* **151** (1987) 403.
16. W. A. JOHNSON and R. F. MEHL, *Trans. AIME* **135** (1939) 416.
17. F. A. SHUNK, in "Constitution of Binary Alloys, 2nd Supplement" (McGraw-Hill, New York, 1969) p. 18.
18. V. M. BERMUDEZ, *Appl. Phys. Lett.* **42** (1983) 70.
19. T. ISEKI, T. KAMEDA and T. MARUYAMA, *J. Mater. Sci.* **19** (1984) 1692.
20. A. PACCAGNELLA, G. OTTAVIANI, P. FABBRI, G. FERLA and S. QUEIROLO, *Thin Solid Films* **128** (1985) 217.
21. G. J. VAN GURP, *J. Appl. Phys.* **44** (1973) 2040.

Received 14 July
and accepted 21 November 1988