JOURNAL OF MATERIALS SCIENCE 25 (1990) 4929–4932

Deposition and characterization of SiC and cordierite thin films grown by pulsed laser evaporation

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Thin films of SiC and cordierite were deposited on Si (1 0 0) by pulsed laser evaporation (PLE) technique at various substrate temperatures. Auger, X-ray photoelectron spectroscopy, and grazing incidence X-ray diffraction were used to investigate the stoichiometry, chemistry, and structure of the PLE-deposited films. The results indicate that properties of SiC films were affected by the substrate temperature. The SiC films grown at 25°C were amorphous and were a physical mixture of silicon, carbon and very little SiC. The films deposited at 500 and 900° C substrate temperature were polycrystalline SiC. The as-deposited cordierite films were stoichiometric crystalline.

1. Introduction

Silicon carbide (SiC) and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) offer great potentials for microelectronic applications. SiC is a high-temperature material which has various microelectronic applications such as light-emitting diodes [1], high-temperature transistors [2], and dielectric isolation [3]. With BeO doping [4], it has a very large thermal conductivity, and high electrical resistivity; and its thermal expansion coefficient is similar to that of silicon. These properties offer SiC the potential for high-speed, high-power, and high-temperature device applications. Cordierite is a multicomponent glass-ceramic material with lower dielectric constant than that of alumina and a low anisotropic thermal expansion coefficient which can be tailored to that of silicon by the addition of mullite [5] in composite form. This material is an attractive alternative to alumina as a packaging and substrate material for high-speed applications.

The deposition of SiC and cordierite thin films has been studied by several investigators. The conventional techniques used usually require either a high substrate temperature during growth or annealing after deposition to achieve stoichiometric crystalline structures. For instance, stoichiometric SiC films were grown by sputtering SiC on to substrates at room temperature, followed by annealing at 1250° C [6]. Reactive sputtering of silicon in methane [7], radio-frequency (r.f.) sputtering [8] and chemical vapour deposition (CVD) [9–12] of SiC all required high substrate temperatures to achieve stoichiometry. Bortz and Ohuchi deposited cordierite-based thin films using a multi-target r.f. sputtering technique [13]. The films were amorphous and near stoichiometric. Subsequent annealing to 1250° C was required to crystallize the film.

The purpose of this study was to determine the feasibility of growing stoichiometric SiC and cordierite films by pulsed laser evaporation (PLE). PLE [14–16] is a technique possessing a number of advantages over conventional film depostion processes. Among these advantages are potential for congruent target evaporation, the capability of growing high-purity films and the relative ease with which even refractory materials, such as SiC and cordierite, can be evaporated.

2. Experimental procedure

The SiC and cordierite thin films were deposited on Si (1 0 0) using the apparatus described previously [17]. The system consists of a deposition chamber which is directly connected to a Perkin-Elmer (PHI) Model 550 X-ray photoelectron spectroscopy/Auger electron spectroscopy (XPS/AES) surface analysis system. A specimen introduction port and transfer arm allow film growth in the deposition chamber and subsequent XPS/AES analysis of the deposited film without air exposure. The base pressure in the deposition chamber was 2×10^{-8} torr, which increased to 1×10^{-7} torr during film growth. The frequency-doubled output (0.53 μm wavelength of a Q-switched Nd:YAG laser (15 nsec pulse duration) was used to evaporate the targets. The target–substrate distance was $\sim$30 mm, and the laser power density was $\sim 9 \times 10^7$ W cm^{-2}. The laser was focused to a 0.9 mm diameter spot at the target and was scanned across the target to produce a uniform film. The targets were CVD beta SiC and hot-pressed cordierite.

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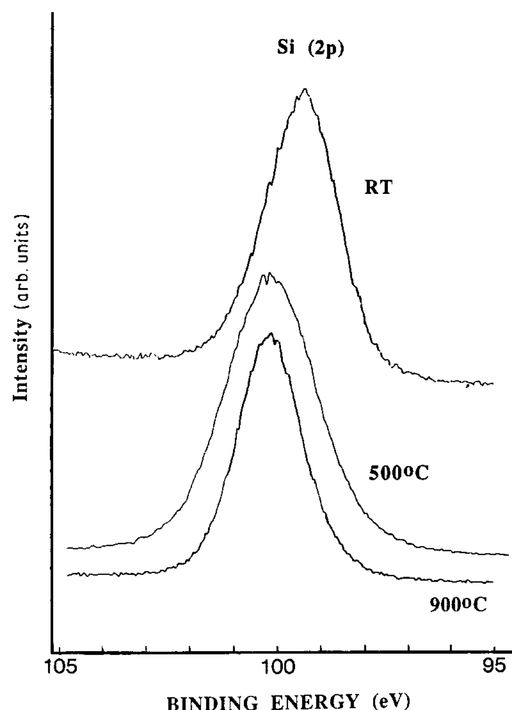


Figure 1 XPS spectra of the Si 2p obtained from SiC films grown at various substrate temperatures.

The SiC films were grown at substrate temperature of room temperature (RT), 500 and 900° C. The substrate temperature was determined by use of a calibrated infrared pyrometer. For cordierite deposition, the substrate was at room temperature.

Grazing incidence X-ray diffraction analysis was done using a Rigaku D/max-1B diffractometer equipped with a thin-film attachment and a monochromator. The angle of incidence of the CuKα X-ray beam was maintained at a glancing angle (ranging from 1° to 10°) while the detector was scanned along 2θ.

3. Results and discussion

3.1. SiC films

The XPS spectra of the Si 2p obtained from SiC films grown at various substrate temperatures are shown in Fig. 1. The RT film exhibits a peak at binding energy of 99.5 eV which corresponds to elemental silicon. The C 1s for this film showed a peak characteristic of carbide at $\sim$282.6 eV along with a tail which can be attributed to graphite. The Si 2p peaks for the 500 and 900° C films show a slight shift to higher binding energy with peak position at $\sim$ 100.2 eV which suggests the formation of SiC. A sharp C 1s peak in carbide form was also observed for these films. The X-ray stimulated Si K L L Auger peak from XPS, as shown in Fig. 2, gives consistent information about the silicon chemical state. Again, the energy shift for 500 and 900° C films as compared to the 25° C films was attributed to the SiC formation.

TABLE I Comparison of modified auger parameters

	α' (eV)
Si (Lit)	1716.1
SiC (RT)	1715.6
SiC (500° C)	1714.9
SiC (900° C)	1714.9
SiC (Lit)	1714.9

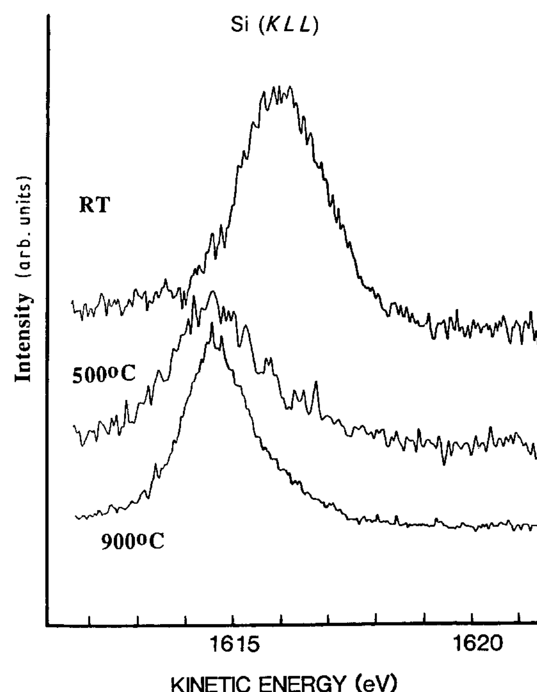


Figure 2 X-ray stimulated Si *kll* Auger peak from XPS.

The modified Auger parameter values for the PLE-deposited films are compared with those published for silicon [18] and SiC [19] in Table I. Since this parameter is independent of any static charging and is characteristic of a particular chemical state, it can provide additional insight into the silicon chemical state. The parameter for the films grown at room temperature has a value of 1715.6 eV which is smaller but closer than that of silicon and is larger than that of the SiC literature value. This suggests that the film has silicon in mostly elemental form with little in SiC form. From the previous C 1s analysis, the film also has carbon in graphite form. The films grown at 500 and 900°C have modified Auger parameters of 1714.9 eV, which is identical to that of SiC reported by Smith and Black [19]. The result of this analysis is in agreement with the previous Si 2p and C 1s analysis of the XPS spectra.

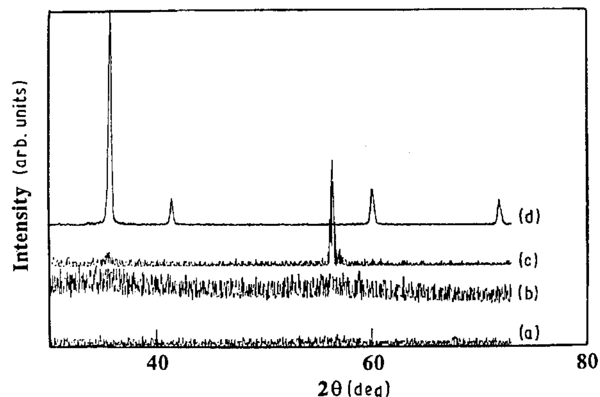


Figure 3 X-ray diffraction patterns for the SiC target and the PLE-deposited films grown at room temperature. (a) Room temperature film, (b) as (a) with 900° C, 30 min anneal, (c) as (a) with 900° C, 150 min anneal, (d) β-SiC target.

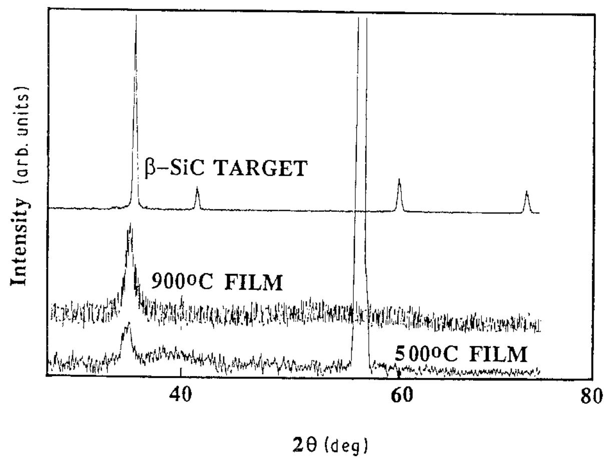


Figure 4 X-ray diffraction patterns for the SiC target and the PLE-deposited films grown at 500 and 900° C substrate temperatures.

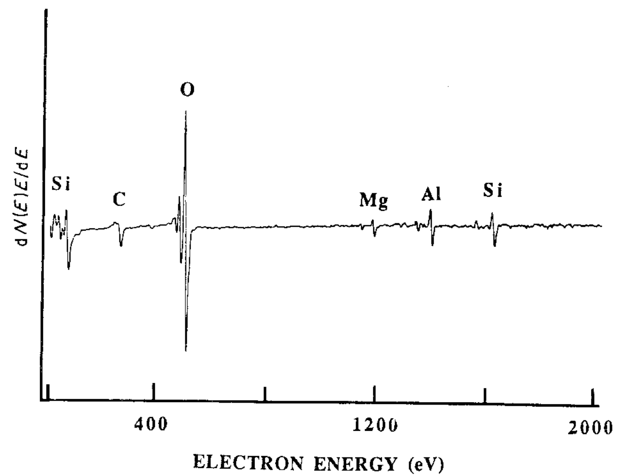


Figure 5 Auger spectrum for the PLE-deposited cordierite film grown at room temperature.

The grazing incidence X-ray diffraction patterns for the SiC target and the PLE-deposited films grown at various substrate temperatures are shown in Figs 3 and 4. From Fig. 3, the film deposited at room temperature is amorphous as compared to the target. Upon subsequent annealing at 900° C for 30 min in argon the film showed a weak peak at 35.6° which corresponds to the most intense peak. The peak intensity increases as the film was annealed for a longer time (150 min total), clearly indicating some SiC crystallization had occurred. This peak was also observed for the films grown at 500 and 900° C substrate temperatures. Fig. 4. The diffraction data and the XPS spectra clearly identify these films as stoichiometric crystalline SiC.

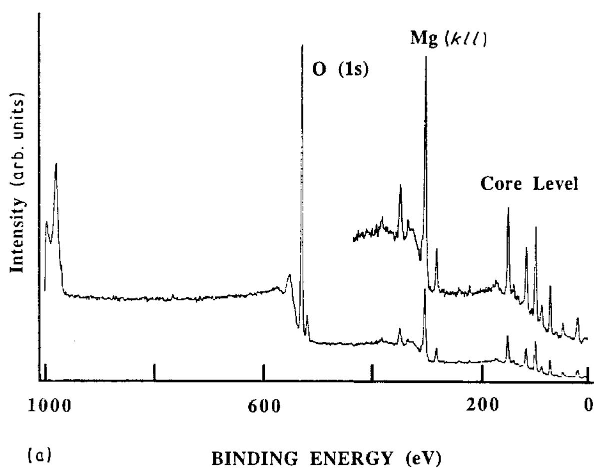
3.2. Cordierite films

The Auger spectrum for the PLE-deposited cordierite film grown at room temperature is shown in Fig. 5. The Auger peak positions as well as peak shapes of magnesium, aluminium and silicon indicate that they are in their oxide forms. An XPS survey spectrum and a high-resolution core-level spectrum of the cordierite film are shown in Figs 6a and 6b. The atomic concentrations of the film constituents can be calculated using the measured 2p photoemission peak height and the published sensitivity factors. The results indicated that the film has approximately the same atomic concentrations of magnesium, aluminium and silicon as the cordierite target.

The X-ray diffraction spectra of the cordierite target and the PLE-deposited film are shown in Fig. 7. A comparison of the two spectra clearly indicates that the film has the same structure as the bulk target. Post annealing of the film is not required because the crystallinity of the target has been preserved in the film.

4. Conclusion

Thin films of SiC and cordierite have been successfully deposited using PLE technique. For SiC growth, the film properties strongly depended on the substrate temperature. From XPS and X-ray diffraction analyses, the film grown at room temperature was amorphous. It consisted of a physical mixture of mostly elemental silicon, graphite carbon, and very little SiC. On the other hand, the films deposited at 500 and 900°C substrate temperatures were stoichiometric. In addition, crystallinity of the films was achieved from PLE alone without subsequent annealing. Thin films of cordierite grown by PLE were also stoichiometric; these films exhibited a crystal structure identical to that of the cordierite target. Again, the films did not require annealing to follow the PLE deposition to achieve crystallinity.



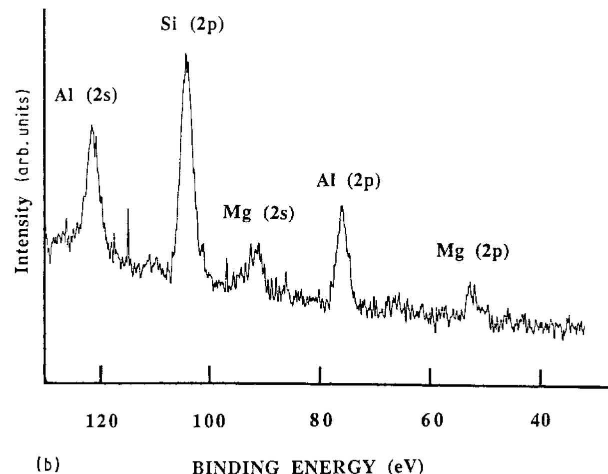


Figure 6 (a) XPS survey spectrum of the cordierite film. (b) High-resolution core-level spectrum of the cordierite film.

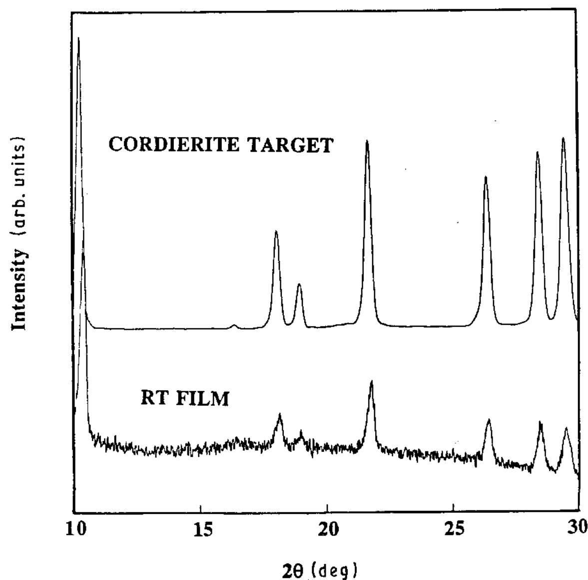


Figure 7 The X-ray diffraction spectra of the cordierite target and the PLE-deposited film.

Acknowledgement

The excellent technical support of David Dempsey and Christopher Schmidt is gratefully acknowledged. This work was sponsored by the Materials Laboratory, Wright Research and Development Center, United States Air Force, Wright-Patterson Air Force Base, Ohio 45433-6533.

References

1. S. NISHINO, A. IBARAKI, H. MATSUNAMI and T. TANAKA, *Jpn. J. Appl. Phys.* **19** (1980) L353.
2. W. V. MUNCH and P. HOECK, *Solid-State Electron* **21** (1978) 479.
3. W.-J. LU, A. J. STECKI, T. P. CHOW and W. KATZ, *J. Electrochem Soc.* **131** (1984) 1907.
4. M. URA and K. NAKAMURA, *Denshizairyo* **21** (1982) No. 9 55 (in Japanese).
5. B. H. MUSSLER and M. W. SHAFER, *Ceram. Bull.* **63** (1984) 5.
6. I. BERMAN, R. C. MARSHALL and C. E. RYAN, Air Force Cambridge Research Laboratories, Technical Report No. 74-0485, October 1974 (NTIS AD787646).
7. A. J. LEARN and K. E. HAQ, *Appl. Phys. Lett.* **17** (1970) 26.
8. T. TOHDA, K. WASA and S. HAYAKAWA, *J. Electrochem. Soc.* **127** (1980) 44.
9. S. NISHINO, J. A. POWELL and H. A. WILL, *Appl. Phys. Lett.* **42** (1983) 460.
10. A. ADDAMIANO and J. A. SPRAGUE, *ibid.* **44** (1984) 525.
11. P. LIAW and R. F. DAVIS, *J. Electrochem. Soc.* **132** (1985) 642.
12. K. SASAKI, E. SAKUMA, S. MISANA, S. YOSHUDA and S. GONDA, *Appl. Phys. Lett.* **45** (1984) 72.
13. M. BORTZ and F. S. OHUCHI, *Thin Solid Films.*
14. H. M. SMITH and A. F. TURNER, *Appl. Opt.* **4** (1965) 147.
15. P. D. ZAVITSANOS and W. E. SAUER, *J. Electrochem. Soc.* **115** (1968) 109.
16. H. SCHWARTZ and H. A. TOURBELLOT, *J. Vac. Sci. Technol.* **6** (1969) 373.
17. P. T. MURRAY, J. D. WOLF, J. A. MESCHER, J. T. GRANT and N. T. McDEVITT, *Mater Lett.* **5** (1987) 250.
18. J. A. TAYLOR, *Appl. Surf. Sci.* **7** (1981) 168.
19. K. L. SMITH and K. M. BLACK, *J. Vac. Sci. Technol.* **A2** (1984) 744.

Received 7 June
and accepted 23 October 1989