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The effects of oxidation on the optical properties of amorphous SiC films

K.B. Sundaram [a], Z. Alizadeh [a], L. Chow [b,*]

[a] *Department of Electrical and Computer Engineering, University of Central Florida, Orlando, FL 32816-2450, USA*
[b] *Department of Physics, University of Central Florida, Orlando, FL 32816-2450, USA*

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Abstract

Amorphous silicon carbide films were deposited by the r.f. sputtering technique using a SiC target. The deposited films were annealed in dry oxygen ambient in the temperature range of 400–700 °C. Optical absorption studies indicated blue shifting effects as the annealing temperature was increased. © 2001 Published by Elsevier Science B.V.

Keywords: Amorphous silicon carbide films; Oxidation; Optical properties

1. Introduction

SiC films can find several applications in the field of high temperature electronics and optical devices because of their high stability. SiC is more stable than Si because of its high melting point and mechanical strength. Oxidation studies are important in SiC technology. A high quality SiO_2 layer is very important in metal-oxide-semiconductors [1]. The oxide layer can be used for several applications, such as surface passivation, dielectric layers in MOS structures, and masks for photolithography processes. The oxidation kinetics of chemically vapor-deposited SiC in dry oxygen and wet oxygen at temperatures between 1200 and 1400 °C have been studied in detail by several authors. Oxidation of polycrystalline SiC films at 1000 °C in an oxygen atmosphere has been reported by Kamimura et al. [2]. Carbone et al. studied the dependence of the optical properties of sputtered hydrogenated amorphous silicon carbide on annealing temperature [3]. Jou et al. investigated the stress behavior of magnetron-sputtered SiC thin films on thermal cycling and annealing [4]. Most of the work is related to annealing studies on epitaxial grown films or single crystals of SiC. One possible application of SiC oxidation is to fabricate broadband optical filters. Low- and high-pass edge filters fall into the category of broadband filters [5]. These filters are characterized by abrupt change between a region of high transmission and a region where light is rejected. Oxidizing SiC at the predetermined temperature can make these edge filters. There is no work reported on oxidation-related studies of amorphous SiC. Hence in the present work, amorphous SiC films were deposited by a r.f. sputtering technique and oxidation was carried out in the temperature range of 400–700 °C. Optical studies were performed on these films to study the effect of annealing on the bandgap shifts.

2. Experimental

The RF sputtering of SiC was carried out in a cryo-pumped vacuum system containing a water-cooled RF magnetron-sputtering gun (US gun II). The sputtering target was powder pressed target of 99.95% purity with dimensions 5 cm diameter × 0.635 cm thick. The target to substrate distance was 3 cm and was kept fixed for all depositions. Argon was used as the sputtering gas for all the depositions with a flow of 10 sccm. The films were deposited onto quartz (silica) substrates. It was found that the optimum condition to achieve the

* Corresponding author. Tel.: +1-407-823-2325; fax: +1-407-823-5112.
E-mail address: lc@physics.ucf.edu (L. Chow).

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best deposition rate were 100 W power and 20 m Torr pressure during sputtering. These sputtering conditions yielded a deposition rate of 80 Å min^{-1}. Identical samples were prepared for both optical as well as thickness measurements. The film was deposited only on half of the sample to provide a step for thickness measurements. These identical samples were then subjected to an oxidation process. The oxidation was carried out in an oxidation furnace using dry oxygen (1 atmosphere) at temperatures ranging from 400 to 700 °C. The oxidation was carried out for 30 min at each temperature. After each oxidation step, the film was brought to room temperature and optical transmission studies were carried out. The films were also annealed in argon and nitrogen ambient under identical conditions to see similar effects of annealing.

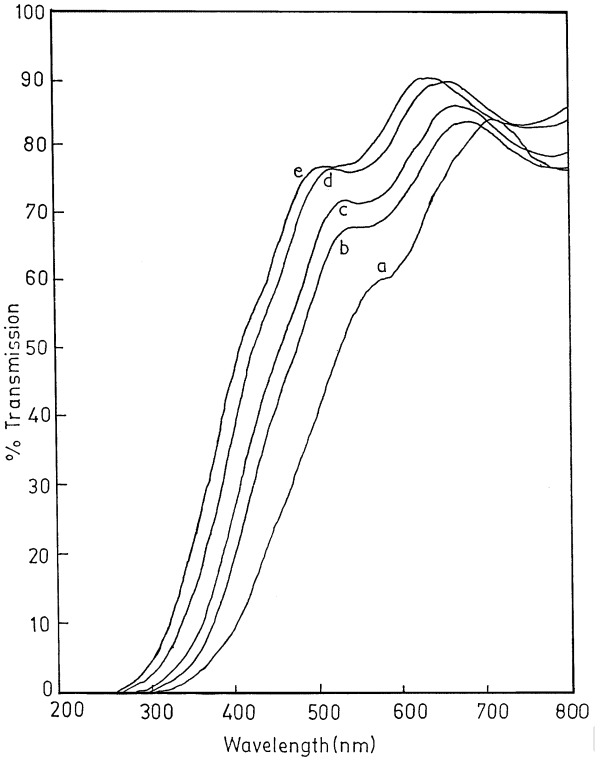

Fig. 1. Optical transmission characteristics of SiC films deposited at different temperatures, (a) as-deposited, annealed in oxygen at (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

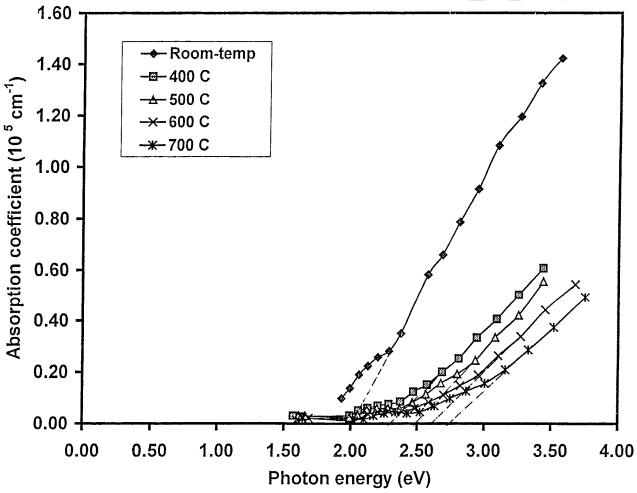

Fig. 2. Graphs of absorption coefficient (α) versus photon energy of SiC films, as-deposited and annealed in oxygen.

The transmission spectra of the SiC films were recorded over the region 190–800 nm using a Carry 3 UV–vis spectrophotometer. The absolute absorption coefficient α was determined directly from the spectrophotometer transmission values for the entire wavelength region. The thickness of the deposited films as well as that of annealed films at each annealing step was measured using a profilometer (Tencor Alpha step). The average deposition rate was calculated by dividing the measured thickness by the sputtering time.

3. Results and discussion

The measured thickness of the as deposited film was found to be 5000 Å. The oxidized films showed a continuous increase in film thickness. The films annealed at 400 and 500 °C showed a thickness increase of 600 Å for each step. Subsequent annealing at 600 and 700 °C showed an increase of 400 Å. In effect the overall film thickness was found to be 7600 Å. This type of increase in thickness was observed for SiC single crystals [6]. It is reported that when a thermal oxide of thickness x is grown, $0.5x$ of the SiC surface is consumed and the excess carbon leaves the sample as CO. The X-ray studies of the as-deposited films as well as of that were subsequently annealed films in different ambients indicated their amorphous nature. Fig. 1 shows the transmission versus wavelength of as-deposited and SiC films annealed in oxygen at temperatures of 400, 500, 600 and 700 °C. The as-deposited film showed more than 80% transmission at 600 nm. The percentage of transmission increased as the oxygen annealing temperature was increased. The film annealed at 700 °C showed a transmission as high as 90% at 600 nm. Fig. 2 shows the absorption versus photon energy for the above films. The optical absorption edge of the films is found to increase with annealing temperatures. The films annealed in argon and nitrogen ambient under identical conditions did not reveal any shifts in the absorption edge. Linear extrapolation yielded a band edge value of 2.0 eV for the deposited film. The other values were 2.26, 2.49, 2.62 and 2.75 eV for the films annealed at 400, 500, 600 and 700 °C, respectively. A similar trend of increasing band gap after annealing was also observed by Fagen [7]. Trapeznikova et al. [8] anealed hydrogenated amorphous SiC films in vacuum in the range of 250–650 °C. They observed a decrease in band gap as the annealing

Table 1
Bandgap evaluation

Annealing temperature (°C)	Increase in thickness (Å)	Oxygen concentration	E_g (eV) from linear approximation	E_g (eV) from optical absorption
400	600	0.107	2.4	2.26
500	1200	0.193	2.6	2.49
600	1600	0.242	2.75	2.62
700	2000	0.285	2.9	2.75

temperature increased. They attributed this due to the effusion of hydrogen during annealing, which causes a large density of structural defects, such as dangling bonds and microvoids. In the present work, the observed blue shift of the band edge is quite surprising. Typically this blue shift can be interpreted as eithe due to (1) the formation of nanocluster of SiC surrounded by SiO_2 and quantum confinement causes the blue shift [9,10], or (2) the homogeneous alloying of amorphous SiC and SiO_2. Since our X-ray data indicated that our films showed amorphous nature even after annealing, we conclude that even though the type of crystal structure of SiC and SiO_2 is quite different, in the amorphous state, the bonding of amorphous SiC and SiO_2 could be quite similar. We postulate that as the amorphous film is annealed in oxygen ambient, the amorphous SiC was oxided and the film gradually becomes a mixture of amorphous SiC–SiO_2. This will cause an increase in band gap as more SiO_2 is formed. This behavior is continuoulsy observed as the films are annealed at progressively higher temperature. The film annealed at 700 °C shows the highest blue shift. To further confirm our postulate, we assume that the oxygen is evenly permeated in to the SiC films. Assuming that the increased thickness of the annealed film is due to the oxygen intake of the film, we calculate the value of oxygen concentration as function of x for the mixture of $SiC_{1-x/2}O_x$. For well-mixed ternary compounds, we can use the average approximation [11] to calculate the average band gap of the compound. For this calculation, the bandgaps assumed were 2.0 eV for SiC and 8 eV for SiO_2, respectively. Assuming a linear increase in bandgap from 2 to 8 eV for the mixture, the bandgaps of different compositions of $SiC_{1-x/2}O_x$ were found, based on the value of x obatained for each annealing step. The results are shown in Table 1. These results are in good agreement with the bandgap energies derived from absorption studies.

4. Conclusion

Amorphous SiC films were sputter deposited on quartz substrates. The films were subsequently annealed in an oxygen ambient at 400, 500, 600, and 700 °C. Optical absorption studies indicated an increase in band gap of the films when subjected to annealing in oxygen ambient. The percentage of optical transmission also increased when the annealing temperatures were increased from 400 to 700 °C in oxygen ambient. It was also observed that the overall thickness of the films increased at each annealing step. The thickness of the grown oxide showed a decreasing trend with increasing temperature, indicating that the oxidation of the SiC films is a diffusion-limited process.

References

[1] S. Zaima, K. Onoda, Y. Koide, Y. Yasuda, J. Appl. Phys. 68 (1990) 6304.
[2] K. Kamimura, T. Kuroda, T. Ogawa, M. Nakao, Y. Onuma, S. Todoroki, Inst. Phys. Conf. Ser. No. 142, Ch. 3, IOP Publishing Ltd., 1995, p. 649.
[3] A. Carbone, F. Demichelis, G. Kaniadakis, J. Non-Cryst. Solids 126 (1991) 139.
[4] J. Jou, L. Hsu, S. Yeh, T. Shyy, Thin Solid Films 201 (1991) 69.
[5] M. Ohring, The Materials Science of Thin Films, Academic Press, New York, 1992.
[6] M.R. Melloch, J.A. Cooper, MRS Spring Meeting, San Francisco, CA, MRS Bulletin, 1997, p. 42.
[7] E.A. Fagen, Optical and electrical properties of amorphous silicon carbide films, 5th International Conference on Amorphous and Liquid Semiconductors (1973), Garmich-Partenkirchen, Germany, Taylor & Francis, Halsted Press, New York, 1974.
[8] I.N. Trapeznikova, O.I. Konkov, V.E. Chinokov, E.I. Terukov, M.P.Vlasenko, Inst. Phys. Conf. Ser. No. 137, Ch. 2, 1993, p. 125.
[9] H. Morisaki, H. Hashimoto, F.W. Ping, H. Nozawa, H. Ono, J. Appl. Phys. 74 (1993) 2977.
[10] S.M. Prokes, W.E. Carlos, O.J. Glembocki, Phys. Rev. B 50 (23) (1994) 17093.
[11] B.G. Streetman, S. Banerjee, Solid State Electronic Devices, 5th ed., Prentice Hall, New Jersey, 2000.