

Optical Absorption in Polymer-Derived Amorphous Silicon Oxycarbonitrides

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Three amorphous silicon oxycarbonitrides are prepared by thermal decomposition of a polymeric precursor at different temperatures. The optical absorption spectra of these materials are measured over a wide range of excitation energies from 0.4 to 5.0 eV. The spectra are analyzed using theoretical models. Two absorption transitions are identified between the deep defect energy level and the delocalized conduction band and between the two delocalized bands. It is found that the band gaps measured decrease with increasing pyrolysis temperature. The results obtained are discussed.

I. Introduction

POLYMER-derived amorphous ceramics (PDCs) prepared by thermal decomposition of polymeric precursors are a new class of multifunctional high-temperature materials.¹ The materials possess a unique structure, which consists of an amorphous matrix made of $\text{SiC}_x\text{N}_y\text{O}_{4-x-y}$ (x, y are integers from 0 to 4) tetrahedra and randomly distributed self-assembled nanosized carbon clusters (named free carbon). A previous study revealed that the conduction mechanism of the materials strongly depends on the concentration of the carbon clusters.^{2–4} When the carbon-cluster concentration is higher than a critical value, the conduction of the materials is controlled by a tunneling-percolation mechanism, resulting in high piezoresistivity. On the other hand, when the carbon-cluster concentration is lower than the threshold value, the conduction of the materials is controlled by the matrix phase, leading to amorphous semiconducting behavior. Such amorphous semiconducting behavior has been widely reported by many researchers, who also showed that the conductivity of PDCs strongly depends on the precursors and processing conditions.^{5–8}

An understanding of the conducting behavior of PDCs requires detailed knowledge of their electronic structures. Given the complex nature of the PDC materials, a theoretical study on the electronic structures of the materials can be very difficult. On the other hand, several techniques, such as optical absorption, are available for studying electronic structures experimentally. Recently, Ferraioli *et al.*⁹ measured the optical absorption spectra of polymer-derived amorphous silicon oxycarbonitrides (SiOCNs) and showed that the Tauc band gap of the materials

decreased with increasing pyrolysis temperature. However, this paper was lacking in a detailed analysis of the spectra.

In this paper, we revisit the optical absorption behavior of SiOCNs. The absorption spectra of these materials are measured over a large range of excitation energy. The spectra obtained are then analyzed using theoretical models to deduce the electronic structures of the materials.

II. Experimental Procedure

The amorphous silicon oxycarbonitride ceramics used in this study are prepared using a commercially available liquid polysilazane (Ceraset, Kion, Huntingdon Valley, PA) as a precursor.¹⁰ First, Ceraset is mixed with 4 wt% of phosphonic acid dimethyl ester. The mixed liquid is then photopolymerized by exposing to a UV lamp of 90 W and a wavelength of 365 nm for 2 h to form solid discs of 600 μm thickness. The discs are then pyrolyzed in a flow of ultra-high-purity nitrogen in a tube furnace to convert them into fully dense SiOCN ceramics. Three kinds of samples are prepared using different pyrolysis temperatures of 1000°, 1200°, and 1300°C for 4 h, respectively. The samples obtained are examined using X-ray diffraction, which reveals that all samples are amorphous without any diffraction peaks.

The SiOCN discs are then ground to powders of $\sim 1 \mu\text{m}$, which are mixed with KBr powder and pressed into disks of 10 mm diameter and 0.5 mm thickness. The ratio of the SiOCN powder to KBr powder is controlled so that the overall absorbance of the discs ranges between 0.2 and 0.8 to optimize the results. The absorption spectra of the SiOCNs are obtained using a UV-3101 double-channel spectrometer (Shimadzu Co., Kyoto, Japan). In order to remove the signal from KBr, two pure KBr disks of the same size are prepared. One is placed at a reference optical channel, and the other is placed at the base line calibrating channel. After measuring the absorption spectra of these two KBr discs, the absorption spectra of the KBr/SiOCN samples are obtained by placing them at the baseline channel. In this way, the absorption spectra obtained from the KBr/SiOCN samples are from the SiOCNs only.

III. Results and Discussion

Figure 1 shows the relationship between absorbance (α) and photon energy ($h\nu$) for the three SiOCNs. To obtain useful information about the electronic structures, these original spectra are compared with theoretical models.

Davis and Mott¹¹ proposed that the absorbance of an amorphous semiconductor as a function of photon energy $h\nu$ at a higher energy range should follow the equation:

$$(\alpha h\nu)^r \propto (h\nu - E_g) \quad (1)$$

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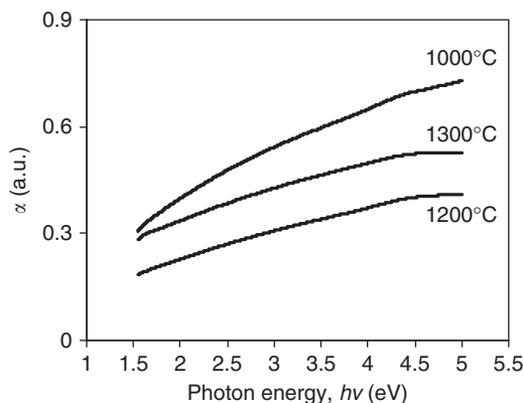


Fig. 1. Room-temperature optical absorption spectra for the amorphous SiOCNs pyrolyzed at different temperatures.

where α is the absorbance of amorphous materials, E_g corresponds to the optical energy gap, and r is the exponent, which can be $1/3$, $1/2$, $2/3$, 1 , and 2 , depending on the transition type in the K space.¹¹ For a direct transition in semiconductor and some amorphous semiconductors,^{12–14} when r takes the value of 2 , the transition will be between the two delocalized bands, and E_g is the optical band gap. The absorption spectra of the SiOCNs are replotted in the form of αhv^2 vs hv (Fig. 2). It can be seen that the absorption over the excitation energy range of 2.5–5.0 eV can be well described by Eq. (1) with $r = 2$. The band gaps for the three SiOCNs are estimated by extrapolation (dashed lines in Fig. 2) to be 2.95, 2.90, and 2.75 eV, respectively (Table I). Previous studies have revealed that depending on their compositions and processing conditions, the optical absorption gaps for amorphous silicon oxide, silicon carbide, and silicon nitride are 8 eV,¹⁵ 2.4–3 eV,¹⁶ and 2.5–4 eV,¹⁷ respectively. The band gaps of the SiOCNs obtained, which consisted of mixed $\text{SiC}_x\text{N}_y\text{O}_{4-x-y}$ tetrahedra, are within these ranges. While it is not our intention to relate the band gap to the network structures of the SiOCNs in this paper, the decrease in the band gap with increasing pyrolysis temperature does suggest structural evolutions with increasing pyrolysis temperature. Such structural evolutions have been widely observed for PDCs.¹⁸

It can be seen from Fig. 1 that the optical absorbance of the SiOCNs is not zero at the lower excitation energy end, and instead increases with increasing excitation energy. This suggests that there should be other absorption mechanisms in the lower excitation energy range. Andronenko and colleagues^{19–21} suggested that for amorphous semiconductors, the optical absorption spectra at a lower excitation energy range should follow

$$\alpha hv = B(hv - E_T)^n \quad (2)$$

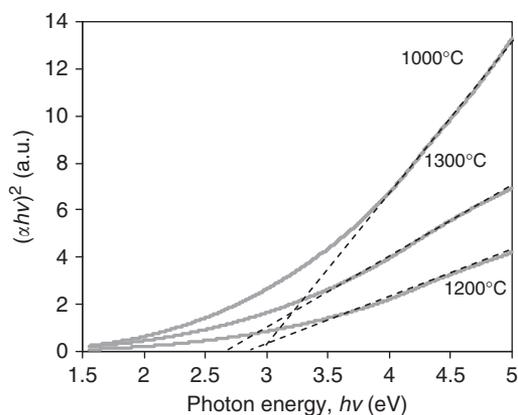


Fig. 2. Plots of $(\alpha hv)^2$ as a function of the photon energy for the three SiOCNs.

Table I. Curve Fit Parameters for the Three SiOCNs

Pyrolysis temperature (°C)	n	E_{Tauc} (eV)	E_g (eV)
1000	1.36 ± 0.05	0.42 ± 0.02	2.95 ± 0.02
1200	1.35 ± 0.05	0.32 ± 0.015	2.90 ± 0.02
1300	1.44 ± 0.02	0.14 ± 0.006	2.75 ± 0.01

This absorption was attributed to the transition from localized states to delocalized states. The n can be either 1.5 or 0.5, depending on the distribution properties of such states.^{19,21,22} E_T is an energy gap and B is a constant. Inkson²³ suggested that for a nonallowed nonvertical transition from a deep impurity trap to a delocalized band, the n should be 1.5. Pfof *et al.*²² also suggested that when n is around 1.5, E_T can be related to the electronic structures of amorphous semiconductors

$$E_T = E_c - E_d \quad (3)$$

where E_c is the edge of the extended conduction band (also called the mobility edge) and E_d is a deep defect level with a high density of state.

In order to check whether there is a transition between the localized defect energy level and delocalized bands in the materials, the absorption behavior of the SiOCNs is measured in the excitation energy range of 0.4–1.8 eV. The data are then analyzed using Eq. (2). It can be seen that the spectra within this excitation range can be well fitted by the equation (Fig. 3). The n values obtained by curve fitting are very close to the theoretical one (Table I). This suggests that the absorption of the SiOCNs over the lower excitation energy range is due to the transition between deep defect states and the mobility edge. It is likely that the deep defect level (E_d) within the SiOCNs is associated with

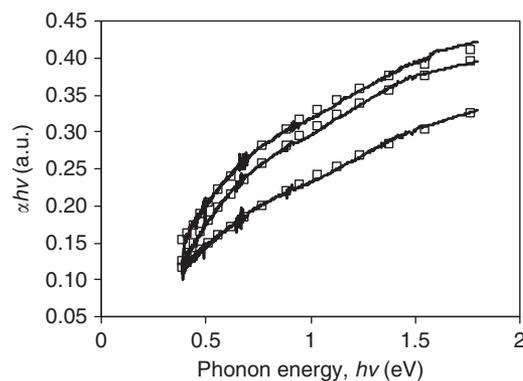


Fig. 3. Plots of αhv as a function of the photon energy for the three SiOCNs. The solid lines are experimental data; the open symbols are curve fits using Eq. (2).

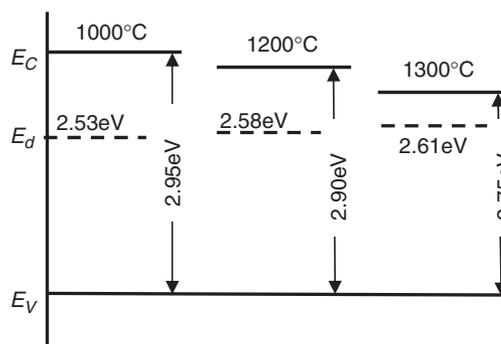


Fig. 4. Schematic showing the electronic structures of the SiOCNs as a function of the pyrolysis temperature.

carbon dangling bands,²⁴ which have unpaired electrons. The band gap of this transition is obtained by curve fitting and is listed in Table I. It can be seen that the band gap significantly decreases with increasing pyrolysis temperature.

Based on the above results, the electronic structures of the SiOCNs can be deduced, which are schematically shown in Fig. 4. It is interesting that the defect-associated state level (E_d) increases with increasing pyrolysis temperature. As the defect level is associated with C-dangling bands, the increase in the level indicates an increase in the concentration of C-dangling bands. Such increases in C-dangling band with pyrolysis temperatures have been widely observed in polymer-derived ceramics.¹³

IV. Conclusion

In this paper, we study the optical absorption behavior of three SiOCN ceramics, which are prepared at different pyrolysis temperatures. The absorption spectra are compared with theoretical models. We find that at lower excitation energies, the absorption is due to the transition of electrons from the C-dangling bond-related deep states to the mobility edge, while at higher excitation energies, the absorption resulted from the transition between the valence band and the conduction band. We also find that the gaps of both transitions decrease with increasing pyrolysis temperature. Such changes are consistent with previously reported structural evolutions of PDCs.

References

- ¹E. Kroke, Y. L. Li, C. Konetschny, E. Lecomte, C. Fasel, and R. Riedel, "Silazane Derived Ceramics and Related Materials," *Mater. Sci. Eng.*, **R26**, 97–199 (2000).
- ²Y. Wang, L. Zhang, W. Xu, T. Jiang, Y. Fan, D. Jiang, and L. An, "Effect of Thermal Initiator Concentration on Electrical Behavior of Polymer-Derived Amorphous SiCN Ceramics," *J. Am. Ceram. Soc.*, **91**, 3971–5 (2008).
- ³L. Zhang, Y. Wang, Y. Wei, W. Xu, D. Fang, L. Zhai, K. Lin, and L. An, "A Silicon Carbonitride Ceramic with Anomalously High Piezoresistivity," *J. Am. Ceram. Soc.*, **91**, 1346–9 (2008).
- ⁴Y. Wang, L. Zhang, Y. Fan, D. Jiang, and L. An, "Stress Dependent Piezoresistivity in Tunneling-Percolation Systems," *J. Mater. Sci.*, **44** [11] 2814–9 (2009).
- ⁵P. A. Ramakrishnan, Y. T. Wang, D. Balzar, L. An, C. Haluschka, R. Riedel, and A. Herman, "Silicoboron–Carbonitride Ceramics: A Class of High-Temperature, Dopable Electronic Materials," *Appl. Phys. Lett.*, **78** [20] 3076–8 (2001).

- ⁶A. M. Hermann, Y. T. Wang, P. A. Ramakrishnan, D. Balzar, L. An, C. Haluschka, and R. Riedel, "Structure and Electronic Transport Properties of Si–(B)–C–N Ceramics," *J. Am. Ceram. Soc.*, **84** [10] 2260–4 (2001).
- ⁷J. Cordelair and P. Greil, "Electrical Conductivity Measurements as a Microprobe for Structure Transitions in Polysiloxane Derived Si–O–C Ceramics," *J. Euro. Ceram. Soc.*, **20**, 1947–57 (2000).
- ⁸C. Haluschka, C. Engel, and R. Riedel, "Silicon Carbonitride Ceramics Derived from Polysilazanes: Part II. Investigation of Electrical Properties," *J. Euro. Ceram. Soc.*, **20**, 1365–74 (2000).
- ⁹L. Ferraioli, D. Ahn, A. Saha, L. Pavesi, and R. Raj, "Intensely Photoluminescent Pseudo-Amorphous SiliconOxyCarboNitride Polymer–Ceramic Hybrids," *J. Am. Ceram. Soc.*, **91**, 2422–4 (2008).
- ¹⁰A. Dhamne, W. Xu, B. Fookes, Y. Fan, L. Zhang, S. Burton, J. Hu, J. Ford, and L. An, "Polymer-Ceramic Conversion of Liquid Polyaluminasilazanes for SiAlCN Ceramics," *J. Am. Ceram. Soc.*, **88** [9] 2415–9 (2005).
- ¹¹E. A. Davis and N. F. Mott, "Conduction in Non-Crystalline Systems: Conductivity, Optical Absorption and Photoconductivity in Amorphous Semiconductors," *Phil. Mag.*, **22**, 903–22 (1970).
- ¹²S. K. J. Al-Ani and A. A. Higazy, "Study of Optical Absorption Edges in MgO–P₂O₅ Glasses," *J. Mater. Sci.*, **26**, 3670–4 (1991).
- ¹³S. T. Kshirsagar and A. P. B. Sinha, "Optical Absorption, Electrical Conductivity and Spectral Response Measurements on the System CdGaSe," *J. Mater. Sci.*, **12**, 1614–24 (1977).
- ¹⁴J. H. Simmons and K. S. Potter, *Optical Materials*. Academic Press, London, 2000.
- ¹⁵P. M. Schneider and W. B. Fowler, "Band Structure and Optical Properties of Silicon Dioxide," *Phys. Rev. Lett.*, **36**, 425–8 (1976).
- ¹⁶I. P. Kaminow, B. G. Bagley, and C. G. Olson, "Measurements of the Absorption Edge in Fused Silica," *Appl. Phys. Lett.*, **32**, 98–9 (1978).
- ¹⁷J. B. Casady and R. W. Johnson, "Status of Silicon Carbide as a Wide-Bandgap Semiconductor for High Temperature Applications: A Review," *Solid State Electron.*, **39**, 1409–22 (1996).
- ¹⁸S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, "Optical Properties of Silicon Nitride Films Deposited by Hot Filament Chemical Vapor Deposition," *J. Appl. Phys.*, **77**, 6534–41 (1995).
- ¹⁹S. I. Andronenko, I. Stiharu, and S. K. Misra, "Synthesis and Characterization of Polyureasilazane Derived SiCN Ceramics," *J. Appl. Phys.*, **99**, 113907 (2006).
- ²⁰P. O'Connor and J. Tauc, "Photoinduced Midgap Absorption in Tetrahedrally Bonded Amorphous Semiconductors," *Phys. Rev. B*, **25**, 2748–66 (1982).
- ²¹P. O'Connor and J. Tauc, "Spectrum of Photoinduced Optical Absorption in a-Si:H," *Solid State Commun.*, **36**, 947–9 (1980).
- ²²D. Pfost, H. Liu, Z. Vardeny, and J. Tauc, "Photo-Induced Absorption Spectra in Ge:H and Si:H," *Phys. Rev. B*, **30**, 1083–6 (1984).
- ²³J. C. Inkson, "Deep Impurities in Semiconductors: II. The Optical Cross Section," *J. Phys. C: Solid State Phys.*, **14**, 1093–101 (1981).
- ²⁴S. Trassl, G. Motz, E. Rossler, and G. Ziegler, "Characterization of Free Carbon Phase in Precursor Derived SiCN Ceramics: q, Spectroscopic Methods," *J. Am. Ceram. Soc.*, **85**, 239–44 (2002). □