

INFRARED REFLECTION SPECTROSCOPY OF AS-ANODIZED AND PASSIVATED 6H AND 4H POROUS SILICON CARBIDE

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ABSTRACT

We present a study of the infrared reflectance of porous silicon carbide (PSC) formed by the electrochemical dissolution of silicon carbide substrates of both 6H and 4H polytypes. The formation of porous silicon carbide from a 4H-SiC substrate is reported for the first time, as is the reflectance from *n*-PSC, both as-anodized and passivated. The passivation of PSC has been accomplished using a short thermal oxidation. Fourier transform infrared (FTIR) reflectance spectroscopy is employed *ex situ* after different stages of the thermal oxidation process. The characteristics of the reststrahlen band normally observed in bulk SiC are altered by anodization; further changes in the reflectance spectra occur following oxidation for different short periods of time. An effective medium theory model which includes air, SiC and SiO₂ as component materials is shown to characterize the observed changes in the reflectance spectra after different stages of PSC oxidation.

INTRODUCTION

The passivation of porous semiconductors by short-term oxidation has been shown to enhance the radiative efficiency of the porous material, increase its structural stability and resistance to further oxidation, and, in some cases, shorten the wavelength of the luminescence spectrum [1]. Porous silicon carbide (PSC) has been of interest recently because it photoluminescences more efficiently than bulk SiC. The thermal oxidation of PSC has been shown to enhance the photoluminescence efficiency markedly and shorten the PL wavelength *vis-à-vis* as-anodized PSC and bulk SiC [2]. Also, PSC oxidizes more slowly under ambient conditions than porous silicon (PS). Therefore, changes in the PSC properties due to high-temperature thermal oxidation can be distinguished more easily from those changes that are due to aging in ambient alone, which permits a well-controlled study of oxide passivation of a porous semiconductor.

Fourier transform infrared (FTIR) reflectance has been used to investigate the nanostructure of PSC nondestructively [3]. As a partially ionic lattice, SiC exhibits nondegenerate longitudinal optical (LO) and transverse optical (TO) phonons in the far infrared portion of the spectrum. The *reststrahlen* band, which is the high reflectance between the TO and LO phonon frequencies, is shown in bulk SiC by the dashed line in Fig. 1. The solid line in Fig. 1 shows the measured *reststrahlen* band in a typical PSC film, which is substantially different than that in bulk SiC. The porous films also have a pronounced peak at 970 cm⁻¹ due to a cavity mode [3].

EXPERIMENTAL PROCEDURE AND RESULTS

A series of PSC films were fabricated from bulk, *n*-type substrates (*n*-PSC) of both 6H and 4H SiC polytypes ($N_D \sim 10^{18}$ cm⁻³) and from *p*-type 6H-SiC substrates (*p*-PSC) ($N_A \sim 10^{18}$ cm⁻³). Nickel films were sputtered onto small areas of each of the *n*-type substrates, and titanium and platinum films onto the *p*-type substrates for electrical contact, and each sample was encapsulated in black wax, exposing only a polished semiconductor area to the electrolyte. The porous layers prepared from *n*-type substrates were anodized in a hydrofluoric acid solution with ethanol (HF:H₂O:CH₃CH₂OH, 1:1:2), and those layers formed from *p*-type substrates were anodized in a dilute hydrofluoric acid solution (HF:H₂O, 1:19). The HF and ethanol were of semiconductor and reagent grade, respectively, and the water was deionized. The films were each prepared under

different galvanostatic conditions for various lengths of time using an EG&G Model 362

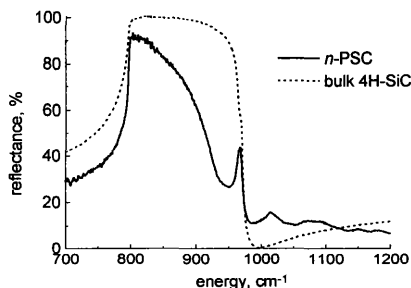


Figure 1. IR reflectance from a 4H *n*-PSC film and bulk 4H-SiC.

The FTIR reflectance spectra were acquired using a Perkin-Elmer Paragon Model 1000 FT-IR spectrometer using a variable angle specular reflectance accessory. The unpolarized reflectance was measured at an angle of 15° (the minimum angle permitted by the instrument) with respect to the normal. The resolution of the spectrometer for these runs is 1 cm⁻¹. Multiple scans were taken for each sample to ensure repeatability, and weak apodization was used.

For the first series of data shown, a single ~10-30 μm thick *n*-PSC film of approximately 1.7 cm² area was formed in *n*-type 4H-SiC in the manner described above. The wafer piece was subsequently diced into eight pieces using a diamond saw. The similar IR reflectance spectra of each piece indicated reasonable

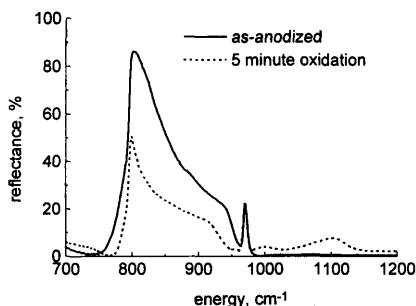


Figure 3. As-anodized and passivated *n*-PSC from 6H-SiC.

Scanning Potentiostat; the *n*-type substrates were also illuminated with an ORIEL 1000 W Hg-Xe lamp during the dissolution process. In addition, the cell bath was recirculated to reduce the adhesion of CO, CO₂ and O₂ bubbles that evolve on the surface of the electrode and to dissipate heat. Following the anodizations, each sample was rinsed in ethanol and dried in air. Some of the samples were then oxidized at atmospheric pressure in an oxidation furnace at 1150° C with dry O₂ flowing at ~2 liters/min. for short intervals of time, and FTIR spectra were acquired on these samples at different stages of the oxidation process.

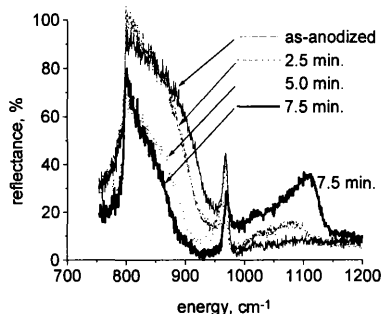


Figure 2. Effects of brief oxidation on *n*-PSC reflectance.

spatial uniformity. Six of these samples were then placed in an oxidation furnace with dry oxygen flowing at 1150° C; one pair of samples was exposed for 2.5 minutes, a second pair for 5 minutes, and a third pair for 7.5 minutes. The spectra from one sample in each of these pairs are shown in Fig. 2. (The spectrum of the other sample was the same as that shown here.) Upon oxidation, the reststrahlen band narrows (decreasing at high frequencies) and changes shape, and a peak at ~1100 cm⁻¹, not seen in bulk SiC and presumably due to SiO₂, becomes more prominent. A second peak at 1016 cm⁻¹ is seen after the anodizations, and more

prominently, after oxidation; it disappears after rinsing the samples in ethanol.

Similar experiments were conducted using $\sim 5\text{ }\mu\text{m}$ thick films of *p*-PSC and *n*-PSC films prepared with 6H-SiC substrates. Following the anodizations, the reflectance was measured within 24 hours prior to and following a 5-minute thermal dry oxidation at 1150°C . The corresponding spectra for each of the *n*-PSC samples are qualitatively similar to those for *n*-PSC formed from 4H material. The spectra of oxidized *p*-PSC samples are, however, quite different from those for the *n*-PSC samples; in particular the reststrahlen band is nearly gone and the SiO_2 peak is quite strong. Representative changes are shown in Figs. 3 and 4. The observation that the change in reflectance of *n*-PSC due to thermal oxidation is small, while the change for *p*-PSC is more pronounced can be understood in terms of the structure of *n*-PSC and *p*-PSC prior to oxidation. The intercore spacing of *n*-PSC is much larger ($\sim 100\text{ nm}$) than that of *p*-PSC ($< 10\text{ nm}$) [2, 4], which is not unlike that of porous silicon prepared from *n*-type and *p*-type material of similarly high doping concentration [5]. Thus, in 5 minutes, an appreciably large portion (if not all) of the crystallite of *p*-PSC is consumed by oxidation (on the basis of available oxidation rate data of 4H-SiC and 6H-SiC [8]), whereas the

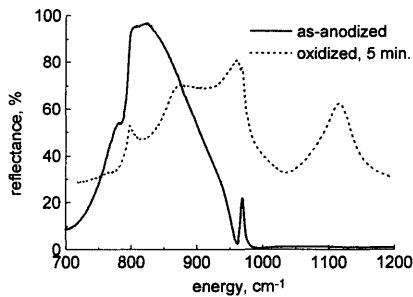


Figure 4. As-anodized and passivated *p*-PSC from 6H-SiC.

the same exposure of an *n*-PSC sample results in the conversion of only a small fraction of the crystallite to oxide.

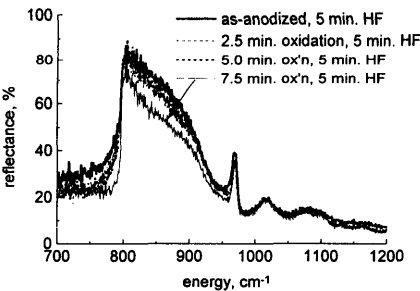


Figure 5. *n*-PSC reflectance following oxide removal in HF.

Following oxidation, one of each of three pairs of samples prepared from 4H-SiC was placed in a solution of 49% HF at room temperature for 5 minutes to etch the oxide. The reflectance of each sample was then measured, which is shown in Fig. 5, along with the spectra from the as-anodized film. Following the HF treatment, the reststrahlen band broadens, but not to the width before oxidation, and the peak near 1100 cm^{-1} gets smaller (see Fig. 2); this broadening is most pronounced for samples oxidized for the longest time.

MODEL

Since the wavelength of light is much larger than the characteristic features of PSC (e.g. pore diameter, intercore spacing), the reflectance from PSC in the reststrahlen band can be understood by modeling the dielectric function of PSC in terms of an effective medium theory. MacMillan, *et al* [3] demonstrated that the cavity Maxwell-Garnett model (C-MG) accounts reasonably well for the general features of the PSC reststrahlen band and is superior to the other effective medium theories they considered. The C-MG model consists of spherical cavities of air ($\epsilon_{\text{air}}=1$)

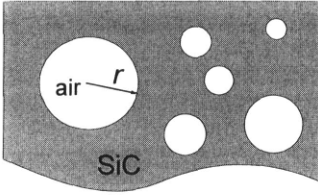


Figure 6a. As-anodized PSC.

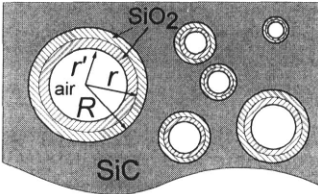


Figure 6b. Oxidized PSC.

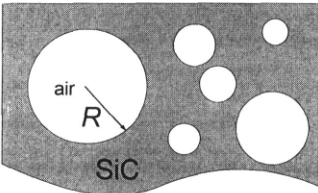


Figure 6c. After removal of SiO₂

surrounded by bulk SiC. The SiC was characterized as a Lorentzian polarizable medium having TO and LO phonon frequencies, a high-frequency dielectric constant, and a damping parameter. In Ref. [3], the experimental data taken on three *p*-PSC samples of different porosity (each having different thickness) yielded slightly different reststrahlen band widths; for higher current densities and increased porosity values, the measured reststrahlen bands were observed to be progressively narrower. It will be shown in a separate publication that the C-MG model does not quantitatively characterize many features of as-anodized and non-oxidized PSC, and needs to be modified. Still, with one modification it is seen here to at least qualitatively characterize the oxidation of PSC.

The infrared reflectance spectrum is modeled at three process stages: (1) after the initial formation of the PSC film (anodization), (2) after a short thermal oxidation of the PSC film, and (3) after etching of the oxide in HF. We assume that the pores are spherical; the appearance of the pores at each of these three stages is shown in Figs. 6a-c. In Fig. 6a, the radius of a typical pore is r , and the volume fraction of air (porosity) is f_{air} . This system of air cavities is the C-MG model used in Ref. [3] and is used to model as-anodized PSC. During oxidation, SiC in the spherical shell from radius r to R is converted to oxide (Fig. 6b). Since the ratio of the molar volume of SiO₂ to that of SiC, g , exceeds one ($g = 2.11$), the radius of the pore decreases to r' as a result of oxidation, where $r'^3 = R^3 - (R^3 - r^3)g$. The dielectric function for such a configuration is [7, 8]

$$\epsilon_{\text{PSC}}(\omega) = \frac{f' A \rho^3 + f' \epsilon_{\text{SiO}_2} B (1 - \rho^3) + \epsilon_{\text{SiC}} (1 - f')}{f' A \rho^3 + f' B (1 - \rho^3) + (1 - f')} \quad (1)$$

where f' is the volume fraction of air and SiO₂, $\epsilon_{\text{SiO}_2}(\omega)$ is the frequency-dependent complex dielectric function of SiO₂ [9], and $\rho = r'/R$; and $A = 3\epsilon_{\text{SiC}}K / (1 - \epsilon_{\text{SiO}_2})$ and $B = (1 + 2\epsilon_{\text{SiO}_2})K / (1 - \epsilon_{\text{SiO}_2})$, where

$$K = \frac{3\epsilon_{\text{SiC}}(1 - \epsilon_{\text{SiO}_2})}{(\epsilon_{\text{SiO}_2} + 2\epsilon_{\text{SiC}})(2\epsilon_{\text{SiO}_2} + 1) - 2(\epsilon_{\text{SiO}_2} - \epsilon_{\text{SiC}})(\epsilon_{\text{SiO}_2} - 1)\rho^3} \quad (2)$$

The new volume fraction of air is $f'_{\text{air}} = g\rho^3 f_{\text{air}} / (g - 1 + \rho^3)$ which is $\leq f_{\text{air}}$. (The effect of strain in the oxide is ignored in this model.) With $\rho = 1$, Equation (1) reduces to the C-MG used after step 1 (and also step 3). If the oxide is totally removed in step 3 (which is not certain), and the SiC is, as expected, essentially unaffected by the HF, the final porosity is $f''_{\text{air}} = g f_{\text{air}} / (g - 1 + \rho^3)$.

We have modeled the reflectance following anodization, oxidation, and oxide removal from both semiinfinite PSC films and PSC films-on-bulk SiC, for a range of PSC film thicknesses. For the reflectance from a 25 μm layer of PSC of 70% initial porosity (roughly corresponding to the

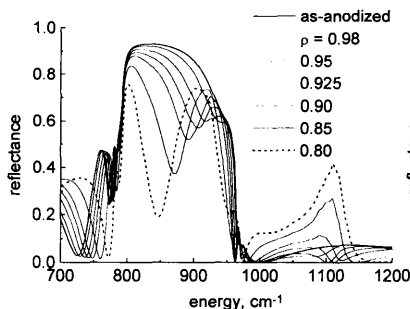


Figure 7. Simulated oxidation of PSC (C-MG model, 25 μm thick PSC).

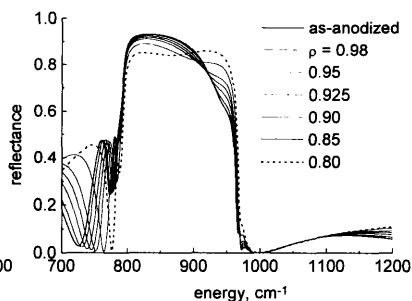


Figure 8. Simulated oxide removal from PSC (C-MG model, 25 μm thick PSC).

experimental data on PSC in 4H-SiC) on an infinite half-space of PSC in air, the course of oxidation (expressed as a decreasing value of ρ , where $\rho=1$ corresponds to the as-anodized sample containing no SiO_2) reveals a narrowing of the reststrahlen band width, as shown in Figure 7. This is consistent with the data in Fig. 2, although the asymmetric shape of the reststrahlen band is not reproduced in this C-MG model. This is accompanied by the appearance of the antisymmetric Si-O stretching mode near 1100 cm^{-1} which is also observed in the data. In the Fig. 8 simulation, the oxide layers have been removed, leaving the spectra corresponding to Fig. 6c. Note that the reflectance of the reststrahlen shoulder on the high-frequency side is increased, as is seen in the data (Fig. 5). It is not clear whether all the oxide is removed during the HF dip. A model that hybridizes the C-MG model with the effective medium model by Looyenga [10] produces the shape of the reststrahlen band better (Figs. 9 and 10, for semiinfinite PSC, $f_{\text{air}} = 0.7$). It will be detailed in a future publication.

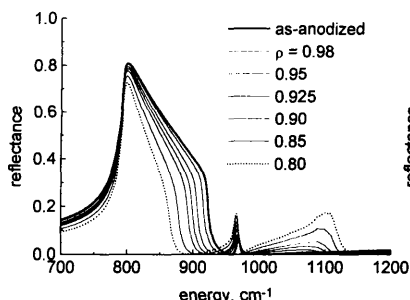


Figure 9. Simulated oxidation (hybrid model, infinite half space PSC).

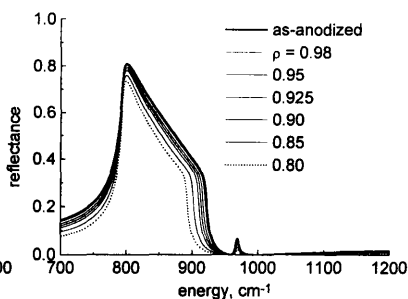


Figure 10. Simulated oxide removal from PSC (hybrid model, infinite half-space PSC).

CONCLUDING REMARKS

We have demonstrated that FTIR reflectance is sensitive to small changes in the PSC composition resulting from a brief thermal oxidation. As for *p*-PSC prepared from 6H-SiC, the IR reflectance spectrum of as-anodized PSC prepared from a 4H-SiC substrate is very different from that of bulk 4H-SiC. For PSC passivated by thermal oxidation, identical oxidation times for *n*-PSC and *p*-PSC material of similar thickness result in different changes in the reflectance spectra, indicative of the size of the pre-oxidation (as-anodized) material. When the C-MG model is extended to support an interfacial oxide layer between the pore and the surrounding SiC, it qualitatively reproduces the general trends observed in experimental data, but does not simulate the shape of the reststrahlen band well. Recent work on a hybrid effective medium model leads to more quantitative agreement with experiment, and may be capable of determining PSC film thickness, porosity, and oxide thickness.

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REFERENCES

1. L. Tsybeskov, S. P. Duttgupta, and P. M. Fauchet, *Solid State Comm.* **95**, 429 (1995).
2. J. E. Spanier, G. S. Cargill III, I. P. Herman, S. Kim, D. Goldstein, A. D. Kurtz, and B. Z. Weiss, in *Advances in Microcrystalline and Nanocrystalline Semiconductors-1996*, edited by R. W. Collins, P. M. Fauchet, I. Shimizu, J.-C. Vial, T. Shimada, A. P. Alivisatos, (Mat. Res. Soc. Symp. Proc. **452**, Pittsburgh, PA, 1997) p. 491.
3. M. F. MacMillan, R. P. Devaty, W. J. Choyke, J. E. Spanier, D. Goldstein, and A. D. Kurtz, *J. Appl. Phys.* **80**, 2412 (1996).
4. J. S. Shor, I. Grimberg, B. Z. Weiss, and A. D. Kurtz, *Appl. Phys. Lett.* **62**, 2836 (1993).
5. R. L. Smith and S. D. Collins, *J. Appl. Phys.* **71**, R1 (1992).
6. Z. Zheng, R. E. Tressler, and K. E. Spear, *J. Electrochem. Soc.* **137**, 854 (1990).
7. L. Genzel and T. P. Martin, *Surface Science* **34**, 33 (1973).
8. J. H. Weaver, R. W. Alexander, L. Teng, R. A. Mann, and R. J. Bell, *Phys. Stat. Sol. (A)*, **20**, 321 (1973).
9. H. R. Philipp, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, New York, 1985) p. 762.
10. H. Looyenga, *Physica* **31**, 401 (1965).