Dielectric relaxation and transition of porous silicon

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Dielectric impedance measurements of porous silicon within the frequency range of 50 Hz–1.0 MHz and temperature range of 298–798 K revealed three semicircles in a Cole–Cole plot when the temperature is raised to 773 K; they are thought to correspond to contributions from the grain interior, grain boundary, and electrode/film interface, respectively. The enhancement in conductivity by heating follows an Arrhenius law with an activation energy transition from 0.07 to 0.79 eV at ~565 K, which originates from band tail hopping that occurs around the Fermi edge. At a critical temperature, a high degree of dispersion in the real and imaginary parts of the permittivity also occurs at low frequencies. This dispersion behavior is interpreted as a combination of electron-lattice polarization associated to the band tail hopping and the crystal field weakening due to thermal expansion. © 2003 American Institute of Physics. [DOI: 10.1063/1.1594821]

INTRODUCTION

Low-dimensional semiconductor structures are of high interest due to their significant technological implications in optics and nanoelectronics. The wide interest in porous silicon (PS) resulted primarily from the proposal,1 in 1990, that there is efficient visible light emission from high porosity structures. Large various numbers of studies have been published on the optical properties of PS.2–4 However, few reports are available in the literature regarding its dielectric performance upon being heated, or characterization of it using an impedance analyzer when the fields are frequency dependent.

Measurement of impedance is important for simultaneous dielectric characterization of materials. The technique has been widely employed to characterize the dielectric behavior of ceramic materials.5 Impedance measurement with respect to frequency allows one to inspect the detailed physical processes inside materials through their electrical analogs.6 In conjunction with structural characterization, impedance analysis yields a complete physical picture of various phenomena occurring in the specimen under different conditions. The most important advantage of impedance measurements is that they can distinguish individual contributions to electrical conduction or to polarization from different sources like the bulk, grain boundaries, intergranular contact regions, and electrode–sample interface regions where defects are generated. This work presents our findings for impedance characterization of complex dielectrics by the so-called Cole–Cole plot, as a function of the temperature along with discussion of possible mechanisms.

EXPERIMENT

The PS samples were prepared on a p-type (100) Si wafers with resistivity of 1–25 Ω cm at room temperature. Electrolyses were performed by an galvanostat in HF:C2H5OH:H2O solution, where the weight ratios were 1:5:4 while the electrolyte, was stirred during the process. The silicon substrates were used as anodes and n-type (111) Si with a resistivity of 0.005–0.02 Ω cm was used as a cathode to obtain a more homogeneous electric field in the electrolyte and this led to samples with very uniform surfaces.7 A current density of 80 mA/cm² was applied for 10 min. After anodization, the PS samples were dried by pentane. The PS layers formed exhibit a red photoluminescence with peak energy at about 2.0 eV under Xe lamp (λ = 458 nm) excitation and the corresponding particle size is about 1.8 nm obtained by matching the measured shift in photoluminescence (PL) with the predicted PL profile8 that matches numerous sets of PL data on PS reported in the literature.

The dielectric measurements were performed in the frequency range of 50 Hz–1.0 MHz and in several stages from room temperature to 573 K in 50 K steps and above 573 K in 25 K steps with an applied potential of 100 mV, using a FLUKE PM-6303 resistance–capacitance–inductance (RCL) meter with a four-wire probe. The temperature was held for 0.5 h prior to each measurement. All the measurements were carried out in atmospheric ambient. Figure 1(a) shows a schematic diagram of this dielectric measurement. Because PS has low conductivity, is lower by several orders of magnitude compared with a Si substrate,9–11 i.e., the resistivity of the Si substrate is much lower than that of PS, the effects of conducting current through the Si substrates on the resistance measured were estimated to be less than 0.1% and thus the effect of the Si substrates could be ignored.12,13 Silver paste was used as an ohmic contact. The samples were then dried at 353 K for 1 h to make the experimental data reproducible.

RESULTS AND DISCUSSION

Relaxation of the impedance can be ideally illustrated with Debye’s expression, where the material is represented by a parallel circuit with a pure resistor \( R \) and a capacitor \( C \). When a Cole–Cole plot is considered, the impedance re-
sponse commonly shows a semicircular form. Figure 2 illustrates the impedance response of the PS sample from room temperature to 798 K. For temperatures below 673 K, complex impedance plots show only one depressed single semicircular arc, indicating that only one primary mechanism, the bulk grain behavior, exists for polarization within the PS film at temperatures below 673 K. The second intercept on the real axis made by the semicircle corresponds to the resistance offered by the bulk grain. As can be observed, with an increase in temperature the intercept of the semicircles shifts towards lower $Z'$ values, indicating reduction of the bulk grain resistance.

When the temperature is increased to 673 K or above, the effects of the grain boundary become more significant by the presence of another overlapping semicircle. The two semicircles at high and low frequencies can be assigned to charge transport within the grain interior and grain boundary effects, respectively. In general, the effect of the grain boundary on the electrical conductivity originates from a grain boundary potential barrier or from space charge layers that are depleted in majority charge carriers and are localized along the grain boundaries. It is found that low frequency semicircular response is dominant with an elevation in temperature compared with the high frequency one, which means that the dominant dielectric relaxation mechanism has changed from bulk grain behavior to grain boundary behavior.

The impedance spectra of the PS exhibit three semicircles when the temperature reaches about 773 K, with the formation of the tertiary semicircle in the low frequency region. When the temperature is increased further, this effect is more evident. We attribute this semicircle to an electrode/film interface effect. In general, the electrode/film effect results from space charge migration. Ionic species with large relaxation times diffuse towards the electrode/film contact region and accumulate there. Polarization of this space charge gives rise to capacitance $C_E$ and corresponding resistance $R_E$.

The Cole–Cole plots demonstrate the dielectric transition from dominance of the grain interior to dominance of the grain boundary at about 673 K, and then to dominance of the electrode/film interface at about 773 K. The transition of a perfect semicircle into an imperfect arc on the left or right may be due to limitation of the equipment, which can only measure frequencies from 50 Hz to 1 MHz.

The high temperature impedance behavior can be described by a series of triple parallel $RC$ circuit elements that correspond to the dielectric behavior of the grain interior, the grain boundary, and the electrode/film interface, respectively, as shown in Fig. 1(b). Since the grain boundary normally exhibits higher resistance than the grain interior and lower resistance than the electrode/film interface, the first semicircle in the high frequency region can be attributed to the behavior of the grain interior while the intermediate and tertiary semicircles in the lower frequency region are attributed to the grain boundary and electrode/film interface. Here the resistor $R$ represents ionic or electronic conduction mechanisms, while the capacitor $C$ represents the polarizability of the PS. The complex impedance $Z'$ measured by the $RCL$ meter can be expressed as

$$Z^* = Z' - jZ'', \quad Z' = \frac{R_B}{1 + \omega^2 R_B^2 C_B^2} + \frac{R_G}{1 + \omega^2 R_G^2 C_G^2} + \frac{R_E}{1 + \omega^2 R_E^2 C_E^2},$$

$$Z'' = \frac{\omega R_B^2 C_B}{1 + \omega^2 R_B^2 C_B^2} + \frac{\omega R_G^2 C_G}{1 + \omega^2 R_G^2 C_G^2} + \frac{\omega R_E^2 C_E}{1 + \omega^2 R_E^2 C_E^2},$$

where $Z'$ and $Z''$ represent the real and imaginary parts of the impedance and $\omega$ is the angular frequency. $R_B$ and $C_B$ are the bulk-grain resistance and capacitance, $R_G$ and $C_G$ are the grain-boundary resistance and capacitance, and $R_E$ and $C_E$ are the electrode/film interface resistance and capacitance, respectively.

One way by which to extract the bulk electrical conductivity $\sigma$ is using

$$\sigma = \frac{l}{R_B A}.$$

The second intercept of the high frequency semicircle with the real axis corresponds to the bulk resistance $R_B$. $l$ is the thickness of the sample (15 $\mu$m) which was measured upon cross section of the sample by scanning electron microscope (SEM); $A$ is the area of the silver electrode (250 mm$^2$). The electrical conductivity of semiconductor materials is usually thermally activated, at least over a limited temperature and follows Arrhenius law,

$$\sigma = A e^{-\frac{E_a}{kT}},$$

where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin.

FIG. 1. (a) Schematic diagram of the dielectric measurement; (b) circuit model for describing the dielectric behavior of PS, where $R_B$ and $C_B$ are the bulk-grain resistance and capacitance, $R_G$ and $C_G$ are the grain-boundary resistance and capacitance, and $R_E$ and $C_E$ are the electrode/film-interface resistance and capacitance, respectively.
\[ \sigma = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right) = \sigma_0 \exp \left( -\frac{E_{TR} - E_F}{k_B T} \right), \]

(3)

where \( \sigma_0 \) is a pre-exponential factor and is characteristics of the material. \( E_{TR} \) is defined as the average energy of the conducting electrons. \( E_a, E_F, k_B, \) and \( T \) are, respectively, the activation energy for conduction, Fermi energy, Boltzmann constant, and absolute temperature. Thus, the activation energy for conduction can be calculated from the slope of the straight line given by least-mean-square analysis of \( \ln \sigma \) vs \( 1000/T \) as shown in Fig. 3(b). The activation energy for conduction is found to have a transition from 0.07 to 0.79 eV at about 565 K. Several researchers have proposed different mechanisms for the conduction transition of materials with a rise in temperature. Landstrass and Ravi\(^{17}\) attributed the transition to the movement of hydrogen and defects from the electrically active deep level to nonactive sites during annealing. Mori \textit{et al.}\(^{18}\) suggested the existence of a surface conductive layer combined with chemical absorption and oxidation. Bharadwaja and Krupanidhi\(^{19}\) proposed that the transition originated from the excitation of charge carriers from a set of shallow traps lying below the conduction band and/or oxygen ion mobility in the interior grains. Axelrod \textit{et al.}\(^ {20}\) correlated the transition to the fractal geometry of PS and to thermally activated relaxation processes from localized and delocalized electronic states of silicon nanocrystals below the Fermi edge. Here we propose this conduction transition behavior of PS originates from band tail hopping that occurs around the Fermi edge, as illustrated in Fig. 3(a). For \( p \)-type PS, the Fermi edge does not lie in the middle of the energy gap but instead shifts towards the valence band because the activation energy obtained is less than half of the band gap derived from the PL measurements. As a result, \( E_{TR} \) does not equal \( E_C \) and the main mechanism responsible for the conductivity is band tail hopping, i.e., the electrons are transported from the Fermi edge to the conduction band tail. The inflexion 565 K can be viewed as the equilibration temperature at which a high temperature equilibrium regime and a low temperature frozen state are separate. The different variation in conductivity for the temperature above and below this critical point is due to changes in the electron concentration. Below the equilibration temperature, the electronic structure of PS is frozen and the density of electrons is constant. Hence \( E_{TR} \) is close to \( E_F \) and the corresponding activation energy is very small. Furthermore, the conductivity prefactor \( \sigma_0 \) is only about \( 2.7 \times 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1} \) as derived from the vertical intercept in Fig. 3(b). When the tem-

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**FIG. 2.** Cole–Cole plots of PS at different temperatures: (a) 298–523, (b) 573–648, (c) 673–723, and (d) 748–798 K. The dots represent the data measured by the RCL meter at different temperatures and the lines correspond to simulation using the \( RC \) parallel circuit model (inset) for typical dielectric materials.
perature is raised above the equilibration temperature, the electrons near the Fermi edge are excited towards higher energy and \( E_{TR} \) shifts into the band tail near \( E_C \) while the Fermi energy is pinned by the defect and dopant states due to the thermal equilibrium regime at every temperature and consequently the shift of the Fermi edge is comparatively small. As a result, the conductivity is activated with much larger activation energy and a prefactor of about 70.3 \( \Omega^{-1} \text{cm}^{-1} \).

Data measured as complex impedance \( Z^* \) can be converted into complex permittivity formalism \( \varepsilon^* \) by the relation

\[
\varepsilon^* = \varepsilon' - j \varepsilon'' = \frac{1}{j \omega C_0 Z^*},
\]

where \( \varepsilon' \), \( \varepsilon'' \), and \( \varepsilon_0 \) represent the real and imaginary parts of the permittivity and the permittivity of vacuum, respectively. \( Z \) is the impedance modulus and \( C_0 \) is the measured vacuum capacitance of the cell and electrodes with an air in place of the sample. Figure 4 illustrates the evolution of the real and imaginary permittivity as a function of the frequency and temperature. When the temperature is raised to 573 K, a high degree of dispersion in the real permittivity

![Figure 3](image1.png)

![Figure 4](image2.png)
occurs at low frequencies. Nobre and Lanfredi\textsuperscript{21} attributed the dispersions to the presence of atomic defects which give the structure great flexibility and the capacity to form solid solutions. Because this dispersion behavior is generally found in dielectrics, in which a conduction hopping-type mechanism is present,\textsuperscript{22} a more reasonable explanation would be that the appearance of band tail hopping at the equilibration temperature causes the large difference in permittivity at temperatures higher or lower than 573 K. The imaginary part $\varepsilon''$ decreases when the frequency increases linearly on a logarithmic scale first and then tends to be constant up to 100 kHz. The imaginary part of the complex permittivity describes the electromagnetic wave absorption, which is responsible for the loss in energy incident waves by electron excitation from the valence to the conduction band, given as\textsuperscript{23,24}

$$\varepsilon''(\omega) = \frac{B}{\omega^2} \int ds \frac{f_{cv}(k)}{|E_c(k) - E_v(k)|},$$

$$E_c(k) - E_v(k) = h\omega = E_G + \hbar^2 k^2/2\mu,$$

where $B$ is a constant. $E_c(k)$ and $E_v(k)$ correspond to energies in the conduction and valence bands at $k$ in reciprocal space. $f_{cv}(k)$ is the intensity of the transition. $\mu = m_e m_h/(m_e + m_h)$ is the reduced mass of the electron-hole pair. $E_G$ and $h$ represent the band gap and Planck constant. For an indirect band gap transition\textsuperscript{25}

$$\varepsilon''(\omega) = A'(T)(h\omega - E_G)^2,$$

where $A'(T)$ containing parameters for the band structure and temperature describes the momentum contribution of phonons to the indirect band gap transition. Considering $h\omega < E_G$ in the frequency range of 50 Hz–1.0 MHz and fitting of the experimental data of imaginary permittivity [Fig. 4(b)] based on the assumption of universal dynamic law,\textsuperscript{26} the equation above can be expressed as

$$\varepsilon''(\omega) = A'(T) \omega^{\alpha - 2} E_G^2,$$

$$B'(T) \omega^\alpha.$$

The exponent $\alpha$ is about $-0.86$ after averaging the calculated exponents at different temperatures. The correlation between $B'(T)$ and the temperature is plotted in Fig. 4(c). It can be observed that there is also a transition at about 561 K which is very similar to the curve of the conduction transition. $B'(T)$ is subsequently expressed in exponential form as $B'(T) = B_0 \exp(-\beta T)$. The coefficient $\beta$ increases from $2.4 \times 10^4$ to $3.0 \times 10^5$ K$^{-1}$ and $B_0$ from $8.8 \times 10^2$ to $1.2 \times 10^5$ at the equilibration temperature. The transition typically suggests the presence of specific polarization phenomenon: lattice and electronic polarization associated to band tail hopping, which contributes to the rapid rise of real and imaginary permittivity above the equilibration temperature. Electron–lattice phonon interaction allows the charge to locally distort the lattice around it and subsequently trap itself in the resulting potential well, which results in the polaron formation.\textsuperscript{21} Moreover, weakening of the crystal field is produced by lattice thermal expansion, which decreases the band gap\textsuperscript{26} which is correlated to the permittivity of semiconductors,\textsuperscript{29–31} may also contribute to this permittivity transition.

**CONCLUSIONS**

The temperature dependence of the complex dielectric behavior of PS exhibits a semicircle in the high frequency region, followed by an intermediate lowest frequency depressed semicircle. These features are attributed to the grain interior, grain boundary, and electrode/film interface contributions. The dielectric transition takes place from dominance of the grain interior to dominance of the grain boundary at about 673 K and then to dominance of the electrode/film interface at about 773 K. The activation energy transition from 0.07 to 0.79 eV at the equilibration temperature, about 565 K, is suggested to be the effect of band tail hopping that occurs around the Fermi edge. When the temperature is raised to this critical temperature, a high degree of dispersion in the real and imaginary parts of the permittivity also occurs at low frequencies. This dispersion behavior is interpreted as a combination of electron-lattice polarization associated to band tail hopping and crystal field weakening due to thermal expansion.