Hopping conduction in SiO_2 films containing C, Si, and Ge clusters

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Temperature dependence of electrical characteristics of SiO_2 films doped with C, Si, and Ge were studied. The conductivity σ was found to vary with the temperature as $\ln\sigma \propto T^{-1/4}$ over a wide temperature range, indicative of the conduction by the variable range hopping (VRH) mechanism. Since the previous optical studies for the same films indicate the existence of clusters in the films, it is very likely that the VRH through localized states associated with clusters dominates the conduction process, irrespective of the kind of group IV elements. © *1996 American Institute of Physics.* [S0003-6951(96)02626-5]

During the past few years, considerable attention has been paid on the strong photoluminescence in the visible region from nanostructures made of group IV elements, such as porous Si,[1] Si,[2–4] and Ge[5] nanocrystals prepared by various methods. Although optical properties of these nanostructures have been widely studied, their electrical transport properties have not been investigated, except for those of porous Si.[6–11] The conduction mechanism of porous Si is attracting much interest because of its possibility of realizing efficient electroluminescent devices. However, porous Si is not an appropriate sample for investigating transport properties of Si nanostructures, because its electrical properties depend highly on the chemical species adsorbed in pores.[7,9,11] In fully understanding the transport properties of nanostructures of group IV elements and realizing various device applications, those of much simpler systems should be studied.

In our previous papers, we have studied SiO_2 films doped with C,[12–14] Si,[15,16] and Ge[17–19] by photoluminescence, Raman and infrared (IR) absorption spectroscopy, and high-resolution transmission electron microscopy (HREM). Our data strongly suggested that these films are the systems of C, Si, and Ge clusters smaller than about 2 nm dispersed in SiO_x matrices. In particular, in HREM studies of Ge doped SiO_2 films, we could directly observe dark patches less than 2 nm corresponding to Ge clusters.[17,18] Although direct observations of C and Si clusters by HREM were not successful due to the background images of SiO_2 matrices, we could demonstrate clear evidences of the cluster formation by Raman spectroscopy.[13–16]

In this letter, we report results of electrical measurements made for these films. The purpose of this work is to extract common electrical properties of nanostructures of group IV elements. We will show that these films generally exhibit $T^{-1/4}$ dependence of $\ln\sigma$, where T and σ are the temperature and conductivity, respectively. This suggests that variable range hopping (VRH) dominates the conduction process, irrespective of the kind of group IV elements. The hopping conduction is believed to be mediated by the localized states associated with the clusters distributed in the films.

SiO_2 films containing C, Si, and Ge clusters were prepared by a rf magnetron cosputtering method described in detail in our previous papers.[12,15,19] Thin plates of C, Si, and Ge of $\sim 5\times 15\times 0.5$ mm^3 in size were placed on a SiO_2 target 10 cm in diameter and they were cosputtered in Ar gas of 2.7 Pa at a rf power of 200 W. The film thickness was set to 200 nm for all the samples. The dopant concentration was controlled by varying the number of the thin plates. Hereafter, we distinguish the samples doped with C, Si, and Ge as $C(n)-SiO_2$, $Si(n)-SiO_2$, and $Ge(n)-SiO_2$, respectively, where n denotes the number of the thin plates. Although exact values of the dopant concentration were not measured, we roughly estimated the concentration by IR absorption spectroscopy[15] and x-ray photoelectron spectroscopy.[19] The dopant concentration in the samples studied in this work is less than 35 vol %.

Prior to the cosputtering, an Al electrode 2 mm wide and 100 nm thick was deposited onto a glass substrate. After the sample deposition, upper Al electrode of the same size was deposited. The upper electrode was arranged to make the right angle with the lower electrode. The active device area is thus 2×2 mm^2. The dc current–voltage ($I-V$) and current-temperature ($I-T$) measurements were made between 100 and 300 K in a closed-cycle type He cryostat (Iwatani Cryomini) by an Advantest R8340 electrometer. The $I-T$ measurements were performed at the applied electric fields of 5×10^4 to 2×10^5 V/cm.

We first present experimental data obtained for $Si-SiO_2$ films and compare them with those of $C-SiO_2$ and $Ge-SiO_2$ films. In order to study conductivity mechanism, it is convenient to plot logarithm of the conductivity, $\ln\sigma$, as a function of $T^{-\alpha}$, and find proper value of α which straightens out experimental curves. We first plotted $\ln\sigma$ as a function of T^{-1} (Arrhenius plot). However, the Arrhenius plot cannot be fitted by a single straight line. This means that carriers are not simply activated to a mobility edge above which extended states exist. On the other hand, $\ln\sigma$ versus $T^{-1/4}$ shown in Fig. 1 are well fitted by straight lines for three samples having different Si concentration [Si(14), Si(24),

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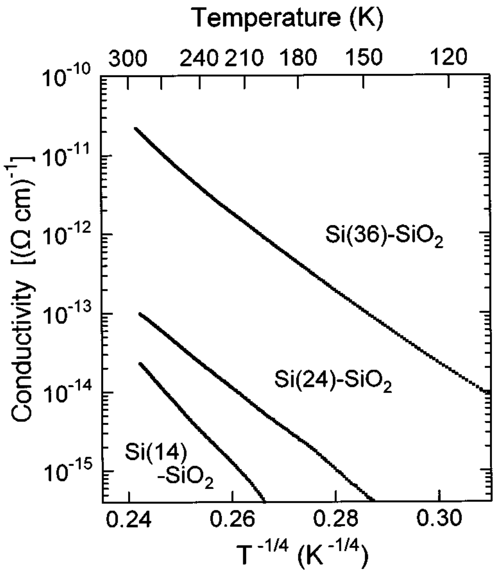

FIG. 1. dc conductivity (in logarithmic scale) as a function of $T^{-1/4}$ for Si–SiO_2 samples having various Si concentrations at an electric field of 5×10^4 V/cm.

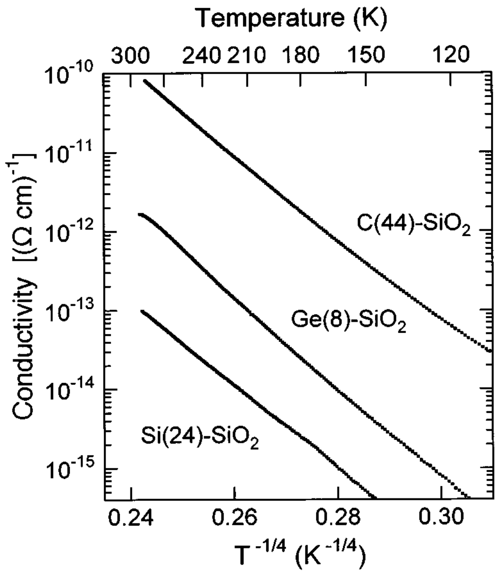

FIG. 2. dc conductivity (in logarithmic scale) as a function of $T^{-1/4}$ for C(44)–SiO_2, Si(24)–SiO_2, Ge(8)–SiO_2 films at an electric field of 5×10^4 V/cm.

and Si(36)–SiO_2]. The $T^{-1/4}$ dependence of $\ln\sigma$ is commonly considered to be a signature of VRH of carriers between localized states near the Fermi level in three dimensions. [20,21]

For thick enough films, the conductivity of VRH can be expressed as[20]

$$\sigma = A\ \exp(-B/T^{1/4}), \tag{1}$$

with

$$B = 2.06[a^3 k_B N(E_F)]^{-1/4}, \tag{2}$$

where A is a constant, k_B is the Boltzmann's constant, $N(E_F)$ is the density of states at the Fermi energy, and a is the decay length of the localized state. Assuming Eqs. (1) and (2), we can determine the values of B from the slope of experimental $\ln\sigma$ versus $T^{-1/4}$ straight lines. Unfortunately, from the values of B only, it is not possible to deduce a and $N(E_F)$ separately. In Fig. 1, we can see that the values of B decrease as the Si concentration increases.

We have performed the same measurements for C–SiO_2 and Ge-SiO_2 films having various C and Ge concentration. The results obtained were very similar to those of Si-SiO_2 films. Figure 2 compares the $\ln\sigma$ versus $T^{-1/4}$ plots obtained for C(44)–SiO_2, Si(24)–SiO_2, and Ge(8)–SiO_2. To facilitate the comparison, we selected samples with similar conductivity. We can see that not only the data for Si–SiO_2 sample but also those for C–SiO_2 and Ge–SiO_2 samples can be very well fitted with the straight lines. This result indicates that the conduction mechanism is generally VRH in the SiO_2 films doped with group IV elements irrespective of the kind of group IV elements.

The VRH requires localized electronic states around the Fermi level. We now consider the origin of the localized states and try to correlate the transport properties with physical structures. In our previous papers,[12–19] we have studied the structures of C–SiO_2, Si–SiO_2, and Ge–SiO_2 films by photoluminescence, Raman, and IR absorption spectroscopy and HREM. Our data strongly suggest that these films are the systems of C, Si, and Ge clusters much smaller than about 2 nm embedded in SiO_x matrices. In particular, we have observed peculiar Raman spectra in Si–SiO_2 systems,[15,16] which were different from those of bulk crystalline Si, amorphous Si, and microcrystalline Si, but very similar to the density of state spectra of Si_{33} and Si_{45} clusters calculated by Feldman *et al.*[22] This result offers a direct evidence of Si clusters smaller than about 2 nm in Si–SiO_2 films. Although the size and size distribution of the clusters are not known, introduction of various size of clusters randomly into SiO_x thin films may generate localized electronic states. If these previous results are taken into account, it is rather straightforward to attribute the presently observed $\ln\sigma$ versus $T^{-1/4}$ behavior to the VRH conduction through the localized electronic states associated with the C, Si, and Ge clusters.

As the Si concentration increases, the slopes (B) of $\ln\sigma$ versus $T^{-1/4}$ straight lines in Fig. 1 decrease. This indicates that $N(E_F)$ and/or a increases with the Si concentration. Since the increases in the Si concentration lead to the increases in the size and/or number of Si clusters, the decreases in B may be attributed to the increase in the size and/or number of Si clusters. The decreases in B with increasing dopant concentrations were also observed for C–SiO_2 and Ge–SiO_2 samples.

In conclusion, we have studied conduction mechanism of SiO_2 films doped with C, Si, and Ge clusters. The temperature dependence of the conductivity could be well fitted by the $\ln\sigma$ versus $T^{-1/4}$ relation. This indicates that the conduction mechanism is generally VRH irrespective of the kind of group IV elements. Since our optical data indicated the existence of clusters in the films, the present VRH conduction is thought to be mediated by the localized electronic states associated with the clusters.

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