Electrical Properties of *tert*-Butyl-Substituted Germanium Cluster

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Conductive amorphous germanium film was prepared by heat treatment of *tert*-butyl-substituted germanium cluster at 200 °C and the crystallization was observed above 500 °C, which are remarkably lower temperatures than those of *n*-propyl-substituted germanium cluster.

Polysilane (polysilylene) and polygermane (polygermylene) are σ-conjugated polymers which have a one-dimensional Si–Si and Ge–Ge chain, respectively. Recently, Sakurai et al.[1] have reported a polysilane dendrimer which has a hyperbranched Si–Si chain with a three-dimensional σ-conjugation.[2–4] A Si/Ge hybrid dendrimer is also synthesized by Sekiguchi et al.[5] The development of the synthesis of such organometallic polymers not only induces the progress of the fundamental studies on low dimensional Si and Ge compounds but also gives a possibility for the application of them. One of the applications of hyperbranched organometallic polymers is to use as a precursor for inorganic materials because the hyperbranched structure enhances the thermal stability and the yield of an inorganic material.[6] In previous papers, we reported the formation of inorganic films using organosilicon cluster (OSI) and organogermanium cluster (OGE) as a precursor.[7–10] The OSI and OGE are prepared from $SiCl_4$ and $GeCl_4$, respectively, by a simple one-pot reaction. We report here the synthesis of *tert*-butyl-substituted Ge cluster and the changes of electrical properties by heat treatment.

The *tert*-butyl-substituted Ge cluster was synthesized in an analogous manner to *n*-propyl-substituted Ge cluster.[9,10] The Ge cluster was prepared as dispersion in THF solution by the reaction of $GeCl_4$ with Mg metal under ultrasonic field. By addition of *tert*-butyl bromide to the solution, Cl groups around the Ge cluster were replaced by *tert*-butyl groups and the *tert*-butyl-substituted germanium cluster was dissolved into the solution. The molecular weight distribution determined by gel permeation chromatography (GPC) analysis is broad one that shows a maxima around 2000 and 7000 with a tail of higher molecular weight than 100000. On the other hand, *n*-propyl-substituted Ge cluster shows a monomodal molecular weight distribution, where M_w and M_w/M_n are 1920 and 1.16, respectively. This difference can be explained by considering that the bulky *tert*-butyl group effectively solubilizes larger Ge clusters in comparison to the *n*-propyl group. By elemental analysis, compositions of *n*-propyl- and *tert*-butyl-substituted Ge clusters are determined to be $Ge_1(C_3H_7)_{1.45}$ and $Ge_1(C_4H_9)_{0.41}$, respectively. Figure 1 shows thermogravimetric (TG) analysis curves for them at a heating rate of 20 °C/min under He. Corresponding to the difference of their compositions, *tert*-butyl-substituted Ge cluster is more thermally stable than *n*-propyl-substituted one. Both show the weight loss in the region of 200–400 °C. The second weight loss region is seen around 800 °C. Thin films of *tert*-butyl-substituted Ge cluster (0.27 μm in thickness) were prepared from a 5 wt% toluene solution by spin coating on a quartz substrate. The films were heat-treated at various temperatures for 30 min in vacuo (10^{-6} torr).

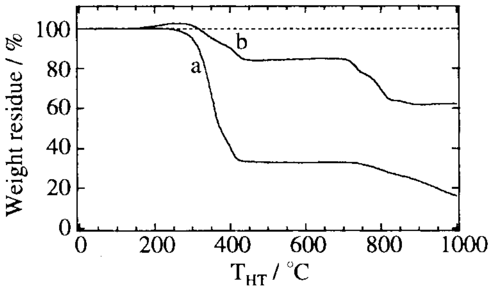

Figure 1. Thermogravimetric curves of (a) *n*-propyl- and (b) *tert*-butyl-substitutedgermanium clusters at a heating rate of 20 °C/min under He.

The Ge–Ge lattice shows a Raman band around 300 cm^{-1}, which is assigned to the transverse optical(TO)-phonon band[9,10] and useful to investigate reconstruction of Ge skeleton during heat treatment. At 200 °C where the thermal decomposition is initiated, a broad Raman band assigned to amorphous Ge (*a*-Ge) was observed at 274 cm^{-1} as shown in Figure 2.

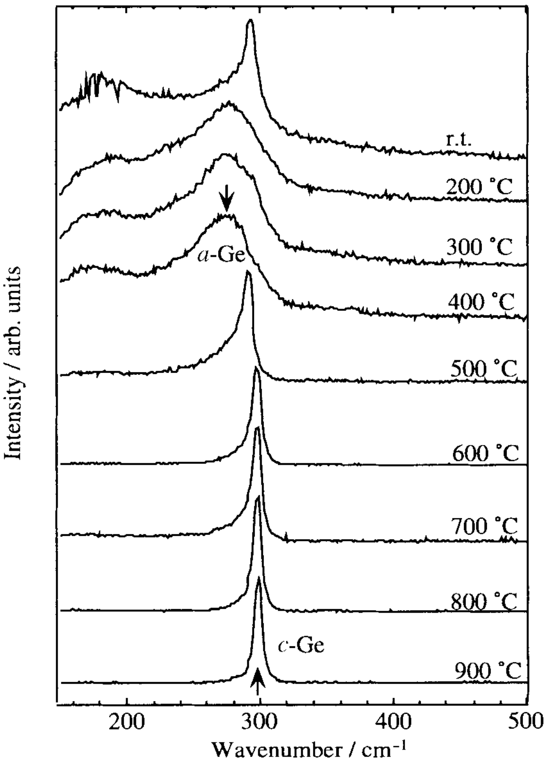

Figure 2. Changes of the Raman band assigned to the transverse optical (TO)-phonon band of Ge by heat treatment in vacuo.

The broadness is caused by the randomness of the bond angle of Ge skeleton. The Raman peaks attributed to Ge–C and C–C stretching bands above 500 cm^{-1} disappeared completely after the heat treatment at 200 °C. Above the thermal decomposition region of 200–400 °C, the TG curves show a plateau in the range from 500 to 700 °C as shown in Figure 1. The overlap of a sharp band at 291 cm^{-1}, which is attributed to crystalline Ge (*c*-Ge), with the broad band of *a*-Ge was observed for the film heat-treated at 500 °C. In the case of *n*-propyl-substituted Ge cluster, the Raman band of *c*-Ge was not observed below 700 °C.[10] This result suggests that the crystallization of Ge skeleton can be enhanced by increasing the size and the Ge composition of the OGE precursor. By increasing the heat treatment temperature, the TO band shows narrowing and the shift to 298 cm^{-1}. The ratio of *a*-Ge to *c*-Ge remarkably decreases above 800 °C, which corresponds to the second weight-loss region in the TG curve. In the temperature region, a disordered moiety may be excluded from crystalline Ge phase.

Figure 3 shows the temperature dependence of conductivity of *tert*-butyl-substituted OGE films heat-treated at various temperatures. Without heat treatment, the OGE film is almost insulator because the σ-conjugation along Ge–Ge chain is isolated by organic substituents and the conduction between the isolated Ge clusters is difficult. The heat treatment induces the elimination of organic substituent and the reconstruction of the Ge–Ge chain, which cause the extension of a three-dimensional Ge network among Ge clusters. In fact, the conductivity increases by 10 orders of magnitude by heat treatment at 200 °C. The highest conductivity is observed at 700 °C because the formation of large crystal grains above 800 °C induces the discontinuity of film.

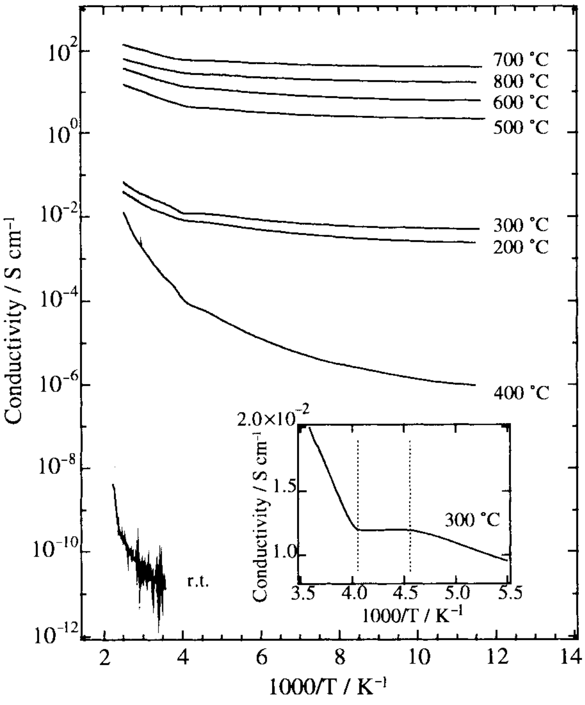

Figure 3. Temperature dependence of conductivities of *tert*-butyl-substituted OGE films heat-treated at various temperatures in vacuo. Au electrodes were vacuum-deposited onto the film through a patterned metal mask, which are shaped in an inter-digitally placed comb-shape configuration.

As shown in the inset of Figure 3, the temperature-dependence curve is divided into three ranges which are attributed to impurity, saturation, and intrinsic ranges from the lower to the higher temperatures. This is a characteristic feature of semiconductors.[11] At 400 °C which is a transition temperature from *a*-Ge to *c*-Ge, the conductivity decreases showing the increase of the activation energy. The higher conductivities are observed above 500 °C because *a*-Ge turns to *c*-Ge as indicated by the sharpness of the Raman band.

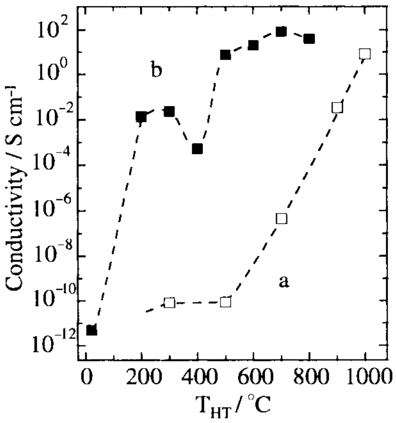

Figure 4. Conductivities of (a) *n*-propyl- and (b) *tert*-butyl-substututed germanium clusters at 20 °C.

In Figure 4, the conductivities measured at 20 °C are plotted against heat treatment temperatures for *n*-propyl- and *tert*-butyl-substituted Ge clusters. The latter shows much higher conductivities than the former, especially at the lower heat treatment temperatures. When the conductivities are compared at 300 °C, the difference is larger than 8 orders of magnitude. The structure of a precursor remarkably influences the properties of an inorganic film.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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