Spatially Selective Formation of Microcrystalline Germanium by Laser-Induced Pyrolysis of Organogermanium Nanocluster Film

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A new method to prepare microcrystalline Ge film by laser-induced pyrolysis of spin-coated organogermanium nanocluster film was developed, which is applicable to the spatially selective formation of microcrystalline Ge micropatterns.

In recent years, the Si–Ge alloy system has received increased attention for possible applications in the semiconductor devices due to its interesting properties. The structural and chemical properties of Si–Ge are similar to Si, which makes this material system compatible with the Si technology.[1] The interest in Ge is stimulated by the application to Si–Ge alloys. In previous papers, we have reported the formation of Si, Ge, and Si–Ge alloys using organo-silicon and germanium nanoclusters as precursors.[2–4] These hyperbranched organometallic polymers have a Si (or Ge) core surrounded by organic side chains, which give the solubility in common organic solvents.[2–7] The inorganic films were prepared by heat treatment of spin-coated films of organo-silicon (or germanium) nanocluster to eliminate the organic side chains. In this paper, we report a new method to form Ge film by combination of organogermanium nanocluster (OGE) and laser-induced pyrolysis technique, where laser-irradiated area of OGE film is converted to microcrystalline Ge (μc-Ge) film with spatial selectivity.

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 detailed procedures are described elsewhere.[4] The molecular weight and the distribution determined by gel permeation chromatography (GPC) analysis are 1130 and 1.14, respectively. By elemental analysis, the composition of the OGE is determined to be $Ge_1(C_4H_9)_{0.78}$. Thin films of OGE (0.27 μm in thickness) were prepared by spin coating on a quartz substrate from a 10 wt% toluene solution. The preheating of the film was carried out at 200 °C for 30 min in vacuo (10^{-6} torr). The color of the thin film changed from pale yellow to brownish yellow after the preheating. Raman spectra were measured by a micro-Raman apparatus with a spectrometer and a liquid nitrogen-cooled charge-coupled device detector. All samples were excited with the 514.5 nm line available from an argon ion laser. A metallograph with an objective (×100) was used for focusing the excitation laser beam on a sample and for collecting the Raman scattering.

The structural changes of the OGE by pyrolysis were studied by Raman spectroscopy. It is known that the transverse optical (TO)-phonon bands of Ge-Ge lattice of amorphous germanium (a-Ge) and crystalline germanium (c-Ge) are observed at 280 and 300 cm^{-1}, respectivelly.[5–8] In Figure 1(a), a shoulder around 280 cm^{-1} is attributed to the a-Ge lattice of the OGE, where other bands are assigned to Ge–C (517 cm^{-1}) and C–C (789, 1170, and 1416 cm^{-1}) bonds. By preheating at 200 °C, the Raman band of a-Ge at 280 cm^{-1} becomes significant accompanying the disappearance of the Raman band above 500 cm^{-1} as shown in Figure 1(b). The unheated and preheated OGE films were irradiated with a 355 nm laser pulse (Nd:YAG laser, FWHM 6 ns). The laser energy density is ca. 60 mJ/cm^2 and the number of the laser pulse irradiation is one. For both films, a sharp Raman band is observed at 300 cm^{-1} as shown in Figure 1(c) and (d). Judging from the Raman band tailing to lower wavenumbers than 300 cm^{-1}, the Raman band should be assigned to that of μc-Ge.

In the case of the unheated precursor film, Raman bands of carbon in the region of 1200 to 1600 cm^{-1} are scarcely observed as shown in Figure 1(c). On the other hand, preheated precursor film shows Raman bands of carbon at 1329 and 1553 cm^{-1} as shown in Figure 1(d). Judging from the broadness of the Raman bands, it is assigned to an amorphous carbon.[7] Such a remarkable difference can be explained by considering the precursor

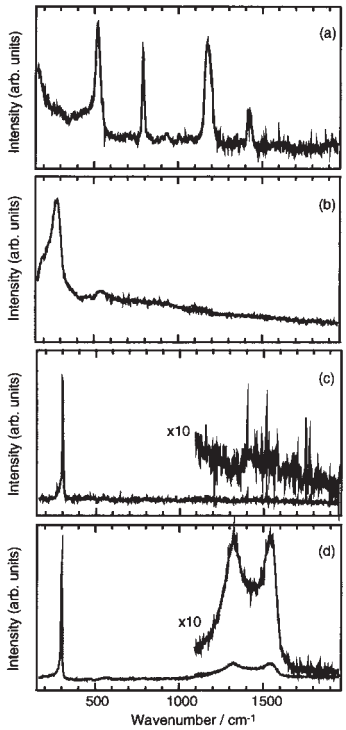

Figure 1. Raman spectra of OGE films unheated (a), preheated at 200 °C (b), laser-induced pyrolyzed without preheating (c), and laser-induced pyrolyzed after preheating at 200 °C (d).

structure. In Figure 1(b), the preheated film shows only a weak Raman band of Ge–C bond at 537 cm^{-1} accompanying the disappearance of the bands attributed to C–C bonds. This must be due to the conversion of *tert*-butyl group to Ge–C network structure because the cross section of the vibration of Ge–C network is very small.[9] The Ge–C structure is expected to be a cross-link structure where carbon enters the germanium network. The laser-induced pyrolysis converted the Ge–C structure to amorphous carbon. Contrary to this, the organic substituent is effectively eliminated and the crystallization of Ge is observed in the case of the laser-induced pyrolysis of unheated OGE film. The Ge–C network structure is the reason why the elimination of the carbon from the preheated precursor film is more difficult than that from the unheated precursor film.

Figure 2(a) and (b) show the optical micrographs of films obtained by laser-induced pyrolysis using unheated and preheated precursor films, respectively. Although the formation of the large grains which correspond to μc-Ge is observed in both cases, the size of the grain is different. The unheated OGE gives lager grain than that of the preheated OGE. This difference is due to the cross-linkage of preheated OGE. The cross-linkage of Ge–C network structure reduces the melting of the precursor film during laser irradiation and then decreases the grain size.

The laser-induced pyrolysis of OGE film is also caused by focusing the CW (continuous wave) laser beam. Figure 2(c) shows the optical micrograph of preheated OGE film irradiated at 514.5 nm line of an Ar ion laser, where the laser beam was focused on the film using an objective lens ($\times$100) with the energy density of ca. 1 MW/cm^2. The horizontal line in the micrograph was drawn by scanning the focused laser beam on the flat precursor

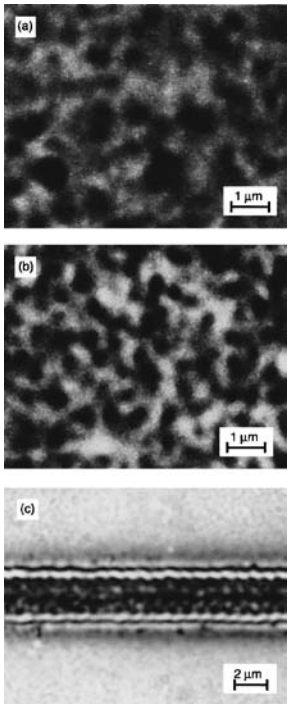

Figure 2. Optical micrographs of films obtained by YAG laser-induced pyrolysis of OGE without preheating (a), by YAG laser-induced pyrolysis of OGE after preheating at 200 °C (b), and by Ar ion laser-induced pyrolysis of OGE after preheating at 200 °C (c).

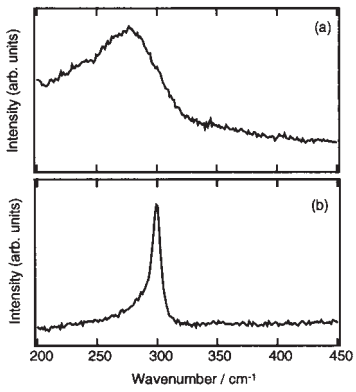

Figure 3. Raman spectra of the film obtained by Ar ion laser-induced pyrolysis of OGE after preheating at 200 °C. (a) unirradiated region, (b) irradiatted region.

film. The width of the line corresponds to the diameter of the focused laser beam. Grains are formed symmetrically around the centerline where the energy density is maximum. The Raman spectra of irradiated and unirradiated regions are shown in Figure 3. In the measurements, the excitation energy density of laser beam was lowered enough to inhibit the laser-induced structural change. The sharp band at 300 cm^{-1} of irradiated region [Figure 3(b)] is assigned to μc-Ge, while broad band at 280 cm^{-1} of unirradiated region [Figure 3(a)] is assigned to a-Ge. This result suggests that spatially selective formation of μc-Ge can be achieved by laser-induced pyrolysis of OGE film. In this preliminarily experiment, a preheated OGE film was used as a precursor because the unheated OGE film (0.27 μm in thickness) has low absorbance at 514.5 nm. The optical densities of the unheated and the preheated OGE films in this study are 0.045 and 0.079 at 514.5 nm, respectively. The optimization of the wavelength of the CW laser beam and the optical instruments enables to depict the micropattern of μc-Ge by scanning the laser beam on the OGE precursor film.

In conclusion, the spatially selective formation of μc-Ge by laser-induced pyrolysis of OGE film is demonstrated. This is a new method to form a micropattern of μc-Ge, and the formation of a micropattern of Si–Ge alloy is expected by laser-induced pyrolysis of spin-coated OGE on Si substrate.

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References and Notes

1 F. Schaffler, *Semicond. Sci. Technol.*, **12**, 1515 (1997).
2 A. Watanabe, M. Unno, F. Hojo, and T. Miwa, *J. Mater. Sci. Lett.*, **20**, 491 (2001).
3 A. Watanabe, M. Unno, F. Hojo, and T. Miwa, *Mater. Lett.*, **47**, 89 (2001).
4 A. Watanabe, M. Unno, F. Hojo, and T. Miwa, *Chem. Lett.*, **2001**, 1092.
5 A. Watanabe, M. Fujitsuka, O. Ito, and T. Miwa, *Jpn. J. Appl. Phys.*, **36**, L1265 (1997).
6 A. Watanabe, M. Fujitsuka, O. Ito, and T. Miwa, *Mol. Cryst. Liq. Cryst.*, **316**, 363 (1998).
7 A. Watanabe, M. Fujitsuka, and O. Ito, *Thin Solid Films*, **354**, 13 (1999).
8 Y.-G. Baek, T. Ikuno, J.-T. Ryu, S. Honda, M. Katayama, K. Oura, and T. Hirao, *Appl. Surf. Sci.*, **1–5**, 7546 (2001).
9 J. Vilcarromero and F. C. Marques, *Thin Solid Films*, **343/344**, 440 (1999).