Fabrication and characterization of a printable semiconductor based on the V$_2$O$_5$–P$_2$O$_5$ system for thermoelectric applications

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A printable semiconductor based on the V$_2$O$_5$–P$_2$O$_5$ system for thermoelectric (TE) applications was fabricated by treatment under reductive conditions. 65V$_2$O$_5$–15P$_2$O$_5$–15CuO–5Fe$_2$O$_3$ ($T_g$=305°C) glass films with a thickness of ~40 μm were prepared on polycrystalline α-Al$_2$O$_3$ substrates via a melt-quenching synthesis, subsequent milling and powder application, and then a viscous flow in air. The glass films heat-treated at 450–650°C in ultra-high vacuum (UHV; ~1 x 10$^{-6}$ Pa) and further reductive hydrogen atmosphere indicated advanced crystallization at the higher temperature, and the reduction demonstrated by the increase of V$^{4+}$/V$^{5+}$ and Cu$^{1+}$/Cu$^{2+}$ ratios. The surface morphology of the crystallized films demonstrated significant crystal growth up to ~5 μm with increased heating temperature in UHV as well as a change in their characteristic shapes. Nano and micropores were homogeneously dispersed throughout the film crystallized at 450°C in UHV, which reduced thermal conductivity. The hydrogen treatment resulted in a volume shrinkage of the precipitated crystals, which is assumed to be due to the reduction and desorption of volatile components. The temperature dependency of the resistivity and the Seebeck coefficient of the crystallized glass-ceramic films were measured. The glass-ceramic films revealed semiconductor behavior in resistivity, and the precipitation in UHV at 650°C decreased the resistivity to 7 x 10$^{-2}$Ωcm at 300°C. A lower resistivity of 2 x 10$^{-2}$Ωcm was obtained after reduction by hydrogen. The films crystallized in UHV at 550 and 650°C had Seebeck coefficients lower than ~120 μV/K and were almost flat in the temperature range 50–300°C. On the other hand, the hydrogen-treated films revealed a Seebeck coefficient of ~+10 μV/K. It is noteworthy that both n- and p-type TE semiconductors were fabricated from the same starting V$_2$O$_5$–P$_2$O$_5$ glass system.

Key-words : Vanadate glass, Glass-ceramics, Composite, Thermoelectric, Printable, Semiconductor, V$_2$O$_5$, P$_2$O$_5$

1. Introduction

Thermoelectric (TE) generation has been recognized as a promising energy-harvesting technology because it enables a direct conversion of thermal energy into electricity, and has less moving parts, and a relatively high output density.1) To date, chalcogenide compounds, such as Bi$_2$Te$_3$ and PbTe-related materials, with a relatively high dimensionless figure-of-merit (ZT > 1) have been commonly used at temperatures up to 800°C.2) However, the TE conversion devices based on these substances have a thermal-to-electric conversion efficiency of only up to ~8% and contain toxic and rare elements in their composition. Thus, the search for alternative nontoxic, stable, and environmentally friendly TE materials is important as well as improving the conversion efficiencies. There is a requirement to increase both the Seebeck coefficient $(S)$ and electric conductivity $(σ)$ while suppressing the thermal conductivity of the materials in order to improve the conversion performance. Considering this fact, several studies have been reported about alternative TE materials, e.g., layered cobalt oxides and heavily doped SrTiO$_3$, and some organic materials, e.g., PEDOT:PSS.3) However, there have been few studies on oxide glass-based TE materials.

An oxide glass generally has a low thermal conductivity due to the disordered amorphous structure, while its electrical resistivity is relatively high. There have been studies on reducing the resistivity by utilizing ionic or proton conduction.8–11) On the other hand, there are also studies on glasses containing multiple transition metal oxides to investigate the transport properties of semiconductor glasses.12–15) Thus, oxide glasses have potential for TE usage by combining these properties of the glass itself or by developing effective composites of low-σ glasses and high-σ nanocrystals. In addition, in comparison with metals or ceramics, an oxide glass is easily molded with macroscopic structure control via a viscous flow, which would be advantageous for large-scale device production.

Vanadate glasses have semiconductor properties such as electrical conductivities of about 10$^5$ Ω$^{-1}$ cm$^{-1}$, owing to the hopping transport of 3d electrons from V$^{4+}$ to V$^{5+}$.16–18) Conduction in these glasses is considered to depend on the V$^{4+}$/V$^{5+}$ ratio according to the general description by the Mott model.17,19,20) The V$_2$O$_5$–P$_2$O$_5$ glasses are considered to have a layered structure comprising VO$_6$, VO$_4$, and PO$_4$ polyhedra; moreover, they exhibit a potential for application in energy devices such as Li-ion batteries as well as other vanadate layered compounds.21) Several studies have also been conducted on utilizing these glasses for switching devices by adding lithium or tellurium22,23) or on controlling the physical properties by doping with transition metals such as Ni, resulting in an alteration of the valence of V-ions.24) In addition, vanadium phosphate glasses have a low glass transition temperature $(T_g)$, which allows applications as sealants for electronic modules by improving the robustness of the glass via Fe or Te doping.25) However, few studies have been conducted regarding
the TE applicability of these V$_2$O$_5$–P$_2$O$_5$ glasses. Fujieda et al. have reported crystallization of these bulk glasses by thermal annealing and microwave treatment in air.$^{26,27}$ Researches on crystallization in more controlled atmosphere and material formation process have been still required to utilize the glass in TE devices.

In this study, we fabricated V$_2$O$_5$–P$_2$O$_5$–CuO–Fe$_2$O$_3$, glass-based TE semiconductors by printing glass films onto $\alpha$-Al$_2$O$_3$ substrates and precipitating conductive oxide crystals. The effects of reductive ambient such as high vacuum and H$_2$ atmosphere and temperature on the precipitating crystalline phases and electrical properties, including the Seebeck coefficient of V$_2$O$_5$–P$_2$O$_5$–CuO–Fe$_2$O$_3$ glass-ceramic films were investigated. In addition, printable formation of oxide glass-based TE materials via application of glass-ink is proposed, which possibly make a contribution to large area device production.

2. Experimental procedures

Figure 1 shows a brief procedure for the sample preparation. The bulk 65V$_2$O$_5$–15P$_2$O$_5$–15CuO–5Fe$_2$O$_3$ glass was first synthesized by a melt-quench process using raw powders of V$_2$O$_5$ powder (99.9% purity, Kojundo Chemical Laboratory), P$_2$O$_5$ powder (>98% purity, Junsei Chemical), Fe$_2$O$_3$ powder (99.9% purity, Kojundo Chemical Laboratory), and CuO powder (99.9% purity, Kojundo Chemical Laboratory). The source materials were mixed in a platinum crucible and heated at 1000°C for 1 h in an electric furnace. The product melts were quenched by pouring onto a stainless steel plate at 150°C. The as-prepared bulk glass was milled into a uniform thickness. The applied glass ink was dried at 140°C for 4.7 wt% of reductive ambient such as high vacuum and H$_2$ atmosphere and temperature on the precipitating crystalline phases and electrical properties, including the Seebeck coefficient of V$_2$O$_5$–P$_2$O$_5$–CuO–Fe$_2$O$_3$ glass-ceramic films were investigated. In addition, printable formation of oxide glass-based TE materials via application of glass-ink is proposed, which possibly make a contribution to large area device production.

The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure. The glass micropowders were applied onto polycrystalline $\alpha$-Al$_2$O$_3$ substrates as an ink using diethylene-glycol-monobutyl-ether-acetate (BCA) and ethylcellulose (EC) as solvent and sintering agent, respectively. The EC was dissolved in BCA at 450°C in vacuum showed crystallization, however, there was also a broad diffraction characteristic to amorphous structure.

3. Results and discussion

Figure 2 represents XRD profiles of the 65V$_2$O$_5$–15P$_2$O$_5$–15CuO–5Fe$_2$O$_3$ glass films on polycrystalline $\alpha$-Al$_2$O$_3$ substrates before and after the heat treatment. The diffraction peaks were identified using ICDD PDF cards for V$_2$O$_5$ (00-034-0187), V$_2$O$_7$ (01-071-0423), V$_2$O$_5$ (01-075-2323, 00-038-1181), V$_2$O$_8$ (01-085-1514, 01-080-2027), V$_4$O$_{11}$ (00-018-1451), V$_6$O$_{13}$ (00-018-1449), V$_8$O$_{14}$ (00-018-1448), VO$_2$ (01-076-0673, 01-076-0456, 01-070-2717, 00-044-0253, 00-042-0876), VO$_3$O$_{13}$ (01-089-0100, 01-075-5982, 01-071-2235), V$_2$O$_3$ (00-027-0940), and V$_2$O$_3$ (01-085-2422, 00-054-0513, 00-041-1426). The powder diffraction data for single oxides was employed for the identification here, excluding hundreds of complex oxides to abbreviate the consideration on valence modification. The plot displayed on the bottom is the XRD pattern of the prepared continuous glass film before crystallization, which exhibited only a broad diffraction characteristic to amorphous structure. The glass film annealed at 450°C in vacuum showed crystallization, however, there was also a broad diffraction on the background indicating existence of reasonable amount of residual glass phase. The diffractions from crystals including V$_{5+}$–V$_{4+}$ were found on the pattern for the film crystallized at temperatures below 550°C. Sharp peaks with higher intensity were detected when annealed at 550°C rather than 450°C, which is also true of V$_2$O$_5$. The crystallization became advanced in the film treated at the higher temperature, that a broad diffraction was hardly observed on the pattern. In addition, there were also diffraction from VO$_2$ and V$_2$O$_3$ found for the film suggesting gradual reduction. On the other hand, the...
treatment at 650°C showed precipitation of VO_2, V_4O_7, and V_2O_5 comprising V-ions with lower valence of ≤V^{2+}, although residual V^{3+} as V_2O_3 and V_2O_5 remained being detected. The heat treatment in H_2 gas demonstrated further reduction of the precipitated crystals. The diffraction pattern revealed crystals with considerably low averaged valence below V^{3.5+} and also V_2O_3 to be the major phases. In addition, metallic Cu possibly emerged by the H_2 reduction, while definite diffraction from Cu_2O crystal was not observed. The significant lower standard energy of formation of V_2O_3 compared with Cu_2O as seen in an Ellingham diagram could explain the cause.

**Figure 3** is a collection of planar SEM images demonstrating the morphological alteration of the films through the crystal precipitation. Figure 3(a) is the surface of a continuous 65V_2O_5$_{-}$15P_2O_5$_{-}$15CuO$_{-}$5Fe_2O_3 glass film after preparation at 315°C in air. The film had a relatively smooth surface owing to the viscous flow of the glass, although there were a few small pinholes found in the film. Figures 3(b)–3(d) show the surface of the glass-ceramic films after thermal treatment in UHV at 450, 550, and 650°C, respectively. Submicron-scale crystals were precipitated in the film treated at 450°C; however, the glassy morphology of the basis film was also observed in the background. The increase in temperature from 550 to 650°C led to significant crystal growth, with the grain shape that is characteristic to crystals clearly seen as well as the appearance of thin whiskers. Figure 3(e) is the surface of the film heat treated at 550°C in a H_2 atmosphere after crystallization at 650°C in UHV. The observed crystals were relatively small or thin in comparison with the surface before the final procedure. This result indicates volume shrinkage due to hydrogen reduction as well as decomposition or desorption of volatile components such as the phosphate component.

**Figure 4** shows the cross-sectional SEM images of the glass-ceramics films on α-Al_2O_3 substrates after thermal treatments. Figure 4(a) is the image of the glass film in which crystals precipitated at 450°C in UHV. There were homogeneously dispersed pores observed in size range of <1μm to ~10μm. Those pores were possibly introduced as bubbles by viscous flow of the glass both in air and UHV, and by ablation of oxygen and phosphates in the reductive ambient. The micro-pores are considered to suppress the macroscopic thermal conduction in the film, which would contribute to enhance the thermoelectric conversion performance. Figure 4(b) exhibits the cross-section of the film after treatment in H_2 at 550°C. It was found the thickness of the glass-ceramics film decreased to ~25μm from 40–50μm of the film after crystallization in vacuum. The result suggests the volume change owing to reduction by hydrogen and desorption, which agree with the morphological change seen on the surface [Fig. 3(e)].

**Figure 5** shows the temperature dependent resistivity of the 65V_2O_5$_{-}$15P_2O_5$_{-}$15CuO$_{-}$5Fe_2O_3 glass-ceramic films after being crystallized by heat treatment at 550°C (□) and 650°C (△), and reduction in H_2 gas at 550°C after being crystallized at 650°C in UHV (△). The resistivity of the films decreased with increasing measurement temperature, indicating that these films have semiconductor conduction characteristics. In addition, the higher crystallization temperature of 650°C in UHV resulted in a decrease in resistivity to 7×10^{-2}Ωcm at 300°C, while a lower value of 2×10^{-2}Ωcm at the same temperature was obtained for the film treated at 550°C in H_2. It is assumed that the reductive ambient atmosphere led to the progressive formation of reduced V^{2+}, V^{3+}, Cu^{1+}, and metallic Cu^{0} in the precipitated crystals as...
suggested in the XRD data, resulted in the improved conductivity. Vanadium oxides including lower valence V-ions reveal metal–insulator transition, for example, V$_2$O$_3$ have a transition temperature around 165 K and reveal metallic conduction even around room temperature. Meanwhile, crystals comprising Cu$^{1+}$ demonstrates relatively lower resistivity in comparison with crystals involving Cu$^{2+}$.\(^{28}\)

**Figure 6** demonstrates the temperature dependent TE property of the Seebeck coefficients measured for the same 65V$_2$O$_5$–15P$_2$O$_5$–15CuO–5Fe$_2$O$_3$ glass-ceramic films. The films crystallized in UHV at 550 and 650°C had coefficients ranging from $-140$ to $-120$ $\mu$V/K, staying almost flat across the measurement temperature range 50–300°C. On the other hand, a Seebeck coefficient of $-140$ $\mu$V/K at 50°C was detected for the film treated in the H$_2$ atmosphere. This value slightly decreased as the temperature increased up to 300°C, which is considered to be caused by the relatively large thermal conduction of this semiconductor film, with heat conduction occurring via charge carrier transport. Note that both n- and p-type TE semiconductors were fabricated from the same starting glass material. I.G. Austin et al. reported about the p-type thermopower of V$_2$O$_3$, meanwhile materials based on Cu$^{1+}$ such as Cu$_2$O are potential p-type semiconductors.\(^{29},^{30}\)

**Figure 7** shows XPS spectra of 65V$_2$O$_5$–15P$_2$O$_5$–15CuO–5Fe$_2$O$_3$ glass film and those after crystallization at respective conditions described above. The O1s peak observed around 533 eV include emissions assigned to OH and H$_2$O. The O1s peak was found to shifted to higher binding energy by crystallizing in high-vacuum and hydrogen; it is considered that the oxygen desorption lead to stronger binding of residual oxygen and surrounding metallic ions. The V$_2$P$_{3/2}$ and V$_2$P$_{1/2}$ satellites due to strong hybridization between V3d and O2p were found between the signals assigned to V$_2$P$_{1/2}$ and O1s, and on the high binding energy side of O1s peak, respectively.\(^{31}\) The spectra for the glass film as-prepared at 550°C revealed V$_2$P$_{3/2}$ and Cu$_2$P$_{3/2}$ peaks assigned to V$^{4+}$ and Cu$^{2+}$ reduced from V$^{5+}$ and Cu$^{2+}$, respectively; the result suggests that surface of the glass particle was reduced by the the EC binder used in the glass-ink.\(^{32}\) On the other hand, for the crystallized films, the ratio of peak areas for sum of V$_2$P$_{3/2}$ against O1s increased along the reducibility due to rising temperature and H$_2$ atmosphere, except for the prepared glass film. This result supports the consideration of oxygen desorption. The heat treatment in higher reduction atmosphere led to relative increase of V$^{4+}$/V$^{5+}$ ratio in the crystallized films indicating the reduction of vanadium oxides, which could be interpreted by the area ratio of corresponding peaks. The similar result was found for the Cu$_2$P$_{3/2}$; a peak assigned to Cu$^{1+}$ or Cu$^{0}$ was detected on the as-prepared glass film, and the relative increment of Cu$^{1+}$ peak through the crystallization was observed in stronger reducing ability. These reduced phases might have decreased the resistivity, but not as low as metals; it is considered those highly conductive components were separately
dispersed in the glass-ceramics film. The result suggests the contribution of low-valence copper oxide as well as vanadium oxides such as non-stoichiometric V$_2$O$_5$ to the semiconductor property and also the p-type conduction. Further investigations on chemical states such as high-resolution XANES analyses are necessary to figure the basis of conduction in this system.

4. Summary

In this study, a V$_2$O$_5$-P$_2$O$_5$ glass-based printable semiconductor was fabricated. 65V$_2$O$_5$-15P$_2$O$_5$-15CuO-5Fe$_2$O$_3$ glass films with $\sim$40$\mu$m thickness were formed on $\alpha$-Al$_2$O$_3$ substrates via the printing of glass ink and a subsequent viscous flow in air. Crystal precipitation was detected after heat treatment at 450°C in UHV, and the progressive crystallization comprising low valence V-ions was observed at the higher temperatures of 550 and 650°C. Further hydrogen treatment at 550°C resulted in reduction and possible occurrence of V$_2$O$_5$ and metallic Cu. The glass-ceramics films which micropores observed may contribute to suppression of the thermal conduction when used in a TE device. The glass-ceramic films revealed the characteristic temperature-dependent resistivity of a semiconductor. The film resistivity was decreased to $7 \times 10^{-2}$Ωcm by crystal precipitation at 650°C in UHV, and further decreased to $2 \times 10^{-2}$Ωcm by successive H$_2$ reduction. In addition, the glass-ceramic films crystallized in UHV demonstrated Seebeck coefficients ranging from $-140$ to $-120$μV/K while that of the film reduced in H$_2$ was $\sim+10$ μV/K. Note that both n- and p-type printable TE semiconductors were fabricated from the same starting V$_2$O$_5$-P$_2$O$_5$ glass system. Increase of the ratios of V$^{4+}$/V$^{5+}$ and Cu$^{1+}$/Cu$^{2+}$ at higher reducing conditions was approved by XPS analysis, although there was an influence of EC binder used in the glass ink at low crystallization temperature. Reduced phases, V$_2$O$_3$ and crystals including Cu$^{1+}$ for examples, are considered to contribute to the decrease of resistivity and the p-type thermoelectric property. Further investigation by separation and individual preparation of single-phase component would clarify the role of each crystal phase. The results of the study would lead to development of practical printable TE devices and large area fabrication in the future.

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