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Seishi Abe

AFFILIATIONS
Research Institute for Electromagnetic Materials, Narita 9-5-1, Miyagi 981-3341, Japan

*e-mail address: abe@denjiken.ne.jp

ABSTRACT
One-step synthesis of the composite thin film with InSb nanocrystals embedded in ZnO doped with Ge was investigated. The films were deposited on water-cooled substrate by radio-frequency sputtering using a target of ceramic ZnO disc with InSb and Ge chips and subsequently heat-treated in vacuum. The composites exhibited a shift in optical absorption edge due to a presence of InSb nanocrystals. Elemental mapping using energy dispersive X-ray microscopy revealed that the added Ge was selectively located in ZnO. The solubility limit of Ge in ZnO was 2 at.% at an annealing temperature of 873 K. Electrical resistivity of the composite was reduced to $6.6 \times 10^{-3} \ \Omega \ cm$ at an annealing temperature of 773 K due to doping with Ge. Simultaneous addition of InSb and Ge to ZnO therefore provided the different functionalities of the optical absorption shifts and relatively low electrical resistivity.

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I. INTRODUCTION

Nanocomposite thin films with narrow-gap-semiconductor nanocrystals embedded in wide-gap host materials are potential application to optoelectronic devices such as infrared detectors and quantum dot solar cells. Optical band gaps of the narrow gap semiconductors shift with respect to crystalline sizes due to quantum confinement effects, indicating that optical absorption edge can be tuned desirably by tailoring the sizes. Wide-gap host materials are generally insulator (e.g., SiO$_2$, Al-O), but carrier transport in an oxide-host was enhanced by employing transparent conductive oxide (e.g., ITO). Hence, the composites should retain the two functionalities of quantum confinement effects in nanocrystals and relatively low electrical resistivity in hosts for such use. In sputtering deposition of nanocomposites, there are typically two ways, using one sputtering target with elemental chips for simultaneous deposition and dual targets for sequential deposition. We’ll focus here on simultaneous deposition (i.e., one-step synthesis) of three materials for nanocrystals, hosts, and dopants to prepare nanocomposites with the valuable functionalities, although this technique usually employs two materials for nanocrystals and hosts.

In our previous study on one-step synthesis of nanocomposites with Ge or InSb nanocrystals embedded in TiO$_2$ host, the nanocrystals phase-separated with TiO$_2$, and optical absorption edges shifted with respect to the concentrations of Ge and InSb. In our preliminary experiments, however, metal (Nb or W) added TiO$_2$ thin films didn’t exhibit obvious decrease in electrical resistivity during heat-treatment at annealing temperatures up to 873 K due to a relatively low crystallinity of TiO$_2$. Although higher temperatures seem to be better for improving the crystallinity, the added Ge in the nanocomposites tended to sublime as an annealing temperature increases even the ranges below 873 K. Hence, we’ll alternatively employ ZnO as a host. ZnO has an energy band gap of 3.37 eV and similar band structure with TiO$_2$. In our preliminary experiment, as-deposited ZnO thin films crystallize with relatively strong (002) orientation even on a water-cooled glass substrate. For doping with impurities, Ge is selected as a n-type dopant, since electrical resistivity was reduced on Ge-doped ZnO thin films. Even though precipitations beyond a solubility limit of Ge in ZnO was occurred, the element Ge would exhibit quantum confinement effects owing to the fact that ZnO/Ge multi-layer provided a shift in an optical absorption edge with respect to Ge concentration. Solubility limits
of Ge in ZnO were altered with respect to preparation techniques (e.g., 0.7 mol% Ge in powder synthesis\textsuperscript{18} and 17 at.% in atomic layer deposition (ALD)\textsuperscript{19}). It is unclear how the present technique (i.e., sputtering deposition and subsequent heat-treatment) provides a solubility limit. Furthermore, an increase of adding Ge finally reaches a production of Zn\textsubscript{2}GeO\textsubscript{4} ternary compound\textsuperscript{18} that is undesirable phase in the current objective. Hence, we’ll choose InSb for nanocrystals as well as the previous study.\textsuperscript{3}

In the present study, we propose a new nanocomposite thin film with InSb nanocrystals embedded in ZnO doped with Ge, and one-step synthesis of the nanocomposite is demonstrated to exhibit different functionalities of quantum confinement effects in InSb nanocrystals and relatively low electrical resistivity in doping with Ge.

II. EXPERIMENTAL PROCEDURE

Simultaneous addition of InSb and Ge to ZnO thin films was prepared on a water-cooled glass substrate (Corning, Eagle XG, Norcross, GA, USA) using radio-frequency (RF) sputtering (Cannon-Anelva, 530H, Kawasaki, Japan) with ceramic ZnO disc (4-in diameter) set on InSb and Ge chips (5×5 cm\textsuperscript{2}). The films were annealed in vacuum for 1h to crystallize the composite. A background pressure was 1.5 × 10\textsuperscript{-7} Torr before introducing argon with gas pressures from 2 mTorr to 11 mTorr. The other preparation conditions were the same to our previous report.\textsuperscript{11}

A structural analysis was performed using the Raman spectrum with a pumping laser at 533 nm (JASCO NRS-5000, Tokyo, Japan) and X-ray diffraction (XRD) with Cu Ka radiation (Rigaku, RAD-X, Tokyo, Japan). An optical transmittance spectrum of the film was measured using UV–vis-NIR spectroscopy (Shimadzu UV3150, Kyoto, Japan), and the composition of the film was analyzed using energy-dispersion spectroscopy (EDS) (EDAX Phoenix, NJ, USA), operating at 10 kV with standard samples of ZnO to calibrate the analyzing results for element Zn and O, with Bi\textsubscript{2}Ge\textsubscript{3}O\textsubscript{12} for elements Bi, and with InSb for elements In and Sb. Photoluminescence (PL) spectrum of the film was measured using an micro-PL system (Horiba LabRAM-HR PL, Kyōto, Japan) at a temperature of 10 K with He-Cd laser at wavelength of 325 nm. The films were observed using scanning transmission electron microscopy (STEM), high-angle annular dark field (HAADF) STEM, and energy dispersive X-ray spectroscopy (EDX) for elemental mapping of O-K, Zn-K, Ge-K, In-L, and Sb-L operating at 200 kV (JEOL ARM200F, Tokyo, Japan). Samples for cross-sectional images were prepared using ion milling. The chemical bonding of the films was measured using X-ray photoelectron spectroscopy (XPS) (Ulvac-PHI, PHI Quantera II, Japan) with Al-K\textalpha radiation.

III. RESULTS AND DISCUSSION

A. Ge-doped ZnO thin films

Prior to investigate simultaneous addition of InSb and Ge to ZnO, we focus on Ge-added ZnO thin films to clarify a solubility limit of Ge in the present technique (i.e., sputtering and subsequent post-annealing). Figure 1 depicts Raman spectra of Ge-added ZnO thin films annealed at 873 K with respect to Ge concentration. At the concentrations below 2.1 at.% Ge, the peaks at 378 cm\textsuperscript{-1}, 438 cm\textsuperscript{-1}, and 593 cm\textsuperscript{-1} are observed, which are assigned to A\textsubscript{1}, E\textsubscript{2}\textsuperscript{high}, and E\textsubscript{1} in LO phonon mode in ZnO,\textsuperscript{20} while a peak at 300 cm\textsuperscript{-1} appears at the concentrations exceeding 3.2 at.% Ge, which is assigned to Ge-Ge optical phonon mode in crystalline Ge.\textsuperscript{21,22}

Figure 2a depicts XRD patterns of Ge-added ZnO thin films annealed at 873 K for 1h in vacuum with respect to Ge concentration. At 0 at.%, single phase ZnO with wurtzite structure is observed with dominant (002) orientation. Addition of Ge exceeding 3.2 at.% produces a different phase of Zn\textsubscript{2}GeO\textsubscript{4} ternary compound with phenacite structure, forming a phase-mixture of ZnO and Zn\textsubscript{2}GeO\textsubscript{4}. Figure 2b depicts lattice constant of Ge-added ZnO thin films annealed at 873 K as a function of Ge concentration. The lattice constant is estimated from the (002) Bragg reflection with strongest intensity in the XRD patterns. The lattice constant first increases with increasing Ge concentration, and then tends to decrease as Ge concentration increases. The film forms single phase at the concentrations below 2.1 at.% Ge, whereas the three phases (ZnO, Ge, and Zn\textsubscript{2}GeO\textsubscript{4}) are contained at the concentrations exceeding 3.2 at.% (Figs. 1 and 2a). Hence, a solubility limit of Ge in ZnO is suggested to be approximately 2 at.% Ge. In the previous reports, powder synthesis provided a solubility limit of 0.7 mol% Ge,\textsuperscript{18} while the ALD technique enlarged a solubility range until 17 at.% Ge in ZnO.\textsuperscript{19} The difference between the both probably depends on whether sample preparation reaches a state in thermal equilibrium or non-equilibrium. Specifically, the Ge\textsubscript{2}Zn\textsubscript{1-x}O powder was synthesized at a relatively high temperature of 1373 K for 6h,\textsuperscript{18} reasonably reaching a thermal equilibrium state. In contrast, the relatively large solubility of 17 at.% Ge in ALD at substrate temperatures up to 623 K in ALD suggests that the deposition technique stands on a state in...
thermally non-equilibrium, because a technique with a state in thermally non-equilibrium (e.g., molecular beam epitaxy) is generally known to enlarge a solubility limit. The present result (i.e., solubility limit of 2 at.%Ge) also suggests that the preparation technique still doesn’t reach thermal equilibrium state.

The present result (i.e., solubility limit of 2 at.%Ge) also suggests that the preparation technique still doesn’t reach thermal equilibrium state.

Figure 3a depicts electrical resistivity of Ge-added ZnO thin films annealed at 873 K for 1h in vacuum as a function of Ge concentration. Pure ZnO thin film (i.e., 0 at.%Ge) has a relatively high electrical resistivity of 1.1 Ω cm, while addition of Ge reduces to 2.6×10^{-3} Ω cm at 1 at.%Ge. Inset depicts optical transmittance spectrum of ZnO thin film containing 1 at.%Ge, which corresponds to the concentrations within the solubility range. An optical absorption edge of ZnO is clearly seen at approximately 370 nm, while infrared transmittance is broadly decreased in the Ge-added ZnO thin film. ZnO thin film containing 1 at.%Ge has a relatively high carrier concentration of 6×10^{11} cm^{-3} with n-type conductivity, which is measured by van der Pauw method. The results suggest that the broad absorption is due to free carriers generated by incorporating Ge into ZnO. Hence, significant decrease in electrical resistivity is due to doping with Ge. Figure 3b depicts PL spectrum at 10 K of Ge-doped ZnO (ZnO:Ge) thin film. Near band emission at 3.38 eV is broadly observed. Compared to pure ZnO thin films, the peak position slightly shifts toward larger energy region due to doping with Ge. Therefore, a solid solution Ge_{x}Zn_{1-x}O thin films are formed in concentrations below approximately 2 at.%Ge.

B. InSb nanocrystals embedded in ZnO doped with Ge

Next, simultaneous addition of InSb and Ge to ZnO is investigated to prepare composite thin films with InSb nanocrystals embedded in ZnO doped with Ge. Figure 4 depicts typical XRD pattern of InSb and ZnO co-added ZnO thin films with respect to the annealing temperature. In this case, the composite contains concentrations of 8.2 at.%InSb and 1.9 at.%Ge in as-deposited state. Although pure ZnO thin films crystallized without heat treatment in our preliminary experiment, the as-deposited composites form amorphous structure. Both InSb and ZnO crystallizes at annealing temperatures exceeding 623 K. Approximately 100 K was lowered in crystallizing temperature in comparison to InSb-TiO_{2} composite.

The XRD peak of InSb maximizes at 773 K, becomes weak as annealing temperature elevates, and finally disappears at 873K with an alternative appearance of In_{2}O_{3}. Figure 5 depicts Raman spectra of the identical specimen. The dashed lines indicate the standard peak positions of Sb with E_{g} Raman mode at 115 cm^{-1} and A_{1g} Raman mode at 150 cm^{-1}.
of InSb with TO Raman mode at 180 cm\(^{-1}\) and LO Raman mode at 190 cm\(^{-1}\).\(^{25}\) The peak of InSb broadly appears at 623 K, becomes obvious at 773 K, and finally disappears at 873 K. This behavior well corresponds to the XRD result (Fig. 4). At relatively high temperatures exceeding 823 K, the peak of Sb with A\(_{1g}\) Raman mode appears and becomes strong at 873 K. Thus, relatively high annealing temperature of 873 K produces Sb (Fig. 5) and In\(_2\)O\(_3\) (Fig. 4) due to partial decomposition of InSb with a melting point of approximately 803 K.\(^{26}\) Therefore, annealing temperatures below 773 K should be employed.

Various phase-appearances in XRD and Raman spectra at an annealing temperature of 773 K is summarized in Fig. 6. Composition ratio Sb/In is indicated using the different colors. We can easily understand a tendency of the phase appearances by focusing on the oxygen concentration. Specifically, amorphous structure forms at a relatively large oxygen concentration irrespective of the InSb concentration. Then, slight decrease in oxygen concentration induces a crystallization of ZnO prior to that of InSb. Further decrease in oxygen produces crystalline InSb and undesirable phases (Sb and Sb\(_2\)O\(_4\)), which disappear as the concentration decreases further. The composite thin film containing crystalline InSb and ZnO (i.e., present objective) can be obtained at the limited range. Further decrease in oxygen concentration produces In\(_2\)O\(_3\), which is also undesirable phase in the present study. Similar crystallization behavior was observed in our previous study on InSb-TiO\(_2\) composite thin film,\(^{11}\) but the composite always included the undesirable phases.

The alternative use of ZnO is therefore useful for no inclusion of In\(_2\)O\(_3\), Sb\(_2\)O\(_4\), and Sb. In addition, Sb deficit from stoichiometry in InSb is smaller than that in InSb-TiO\(_2\) (i.e., a minimum ratio of 0.6 in Sb/In in the present study in contrast to below 0.4 in TiO\(_2\)).

It is unclear where the co-added Ge locates in the InSb-ZnO composite thin film, since there is no peak of element Ge in the XRD patterns and Raman spectra (Figs. 4 and 5). Figure 7 presents HAADF-STEM cross section image of the composite thin film containing 9.24 at.%InSb and 1.85 at.%Ge. Slightly bright grains distribute in whole area. High resolution image is presented in Fig. 8a. The slightly bright area indicates presence of In (Fig. 8e) and Sb (Fig. 8f) in EDX elemental mapping, reasonably forming a compound semiconductor InSb. The other dark area in Fig. 8a indicates presence of Zn (Fig. 8c) and O (Fig. 8b), reasonably forming an oxide semiconductor ZnO. The added Ge is suggested to be located in ZnO, since the distribution of Ge in the elemental mapping (Fig. 8d) is similar to those in Zn (Fig. 8c) and O (Fig. 8b). Therefore, the added Ge selectively locates in ZnO crystal. Figure 9 presents high resolution TEM cross-section image of the identical
area. The white circle with label b) corresponds to the phase containing In and Sb in elemental mapping (Fig. 8e and 8f), and the circle with label c) corresponds to the phase containing Zn, O, and Ge (Figs. 8b, 8c, and 8d). Fast Fourier Transform (FFT) analysis of the label b) is presented in Fig. 9b. Plane widths are estimated to be 0.371 nm in label A, 0.229 nm in B, and 0.372 nm in C with angles of 35 deg in A-O-B, 71 deg in A-O-C, and 35 deg in B-O-C. The spots are assigned to (11-1), (20-2), and (1-1-1) in cubic InSb. FFT analysis of the label c) (Fig. 9a) is presented in Fig. 9c. Plane widths are estimated to be 0.276 nm in label A, 0.191 nm in B, and 0.193 nm in C with angles of 67 deg in A-O-B, 108 deg in A-O-C, and 41 deg in B-O-C. The spots are assigned to (01-10), (10-1-2), and (1-10-2) in hexagonal ZnO. The elemental mapping suggested that the added Ge locates in ZnO phase (Fig. 8d), but any other phases can’t be seen in the ZnO phase, reasonably forming a solid solution of Zn$_{1-x}$Ge$_x$O. The film therefore forms a nanocomposite with InSb nanocrystals embedded in ZnO containing Ge.

Figure 10a depicts electrical resistivity of the nanocomposite thin film containing 8.24 at.%InSb and 1.85 at.%Ge with respect to annealing temperature. The electrical resistivity is reduced significantly from high values beyond the measurable range of our equipment (exceeding $10^3 \, \Omega \, \text{cm}$) to $6.6 \times 10^{-3} \, \Omega \, \text{cm}$. The inset depicts optical transmittance spectrum of the film annealed at 773 K. Optical transmittance of a pure ZnO is presented for comparison. The nanocomposite reduces the infra-red transmittance, reasonably due
to an absorption by free carriers generated from Ge incorporated into ZnO crystal. In addition, optical absorption edge at ultra violet part in pure ZnO shifts toward longer wavelength region due to a presence of InSb nanocrystals. Figure 10b shows the XPS spectrum of the nanocomposite thin film. The main peak is located at a binding energy of 32.4 eV that corresponds to the 3d spin state of Ge⁴⁺, while the peak of metallic state Ge⁰ is negligible. Hence, the doped Ge has an ionized state with quadrivalent. Figure 10c depicts XRD pattern of the identical specimen. All of the diffraction peaks are assigned to both InSb and ZnO. Raman spectrum indicates a peak of InSb with TO mode (not shown). Therefore, the nanocomposite actually consists of InSb nanocrystals embedded in ZnO doped with Ge.

Simultaneous addition of InSb and Ge to ZnO has provided the different functionalities; i) shifting optical absorption edge due to the presence of InSb nanocrystals, which are phase-separated with ZnO, and ii) reducing electrical resistivity due to a dopant Ge, which forms a solid solution with ZnO. To exhibit the noteworthy functionalities in one-step synthesis, following requirements should be satisfied:

(i) phase-separation and solid solution selectively take place in a composite.
(ii) host materials are well crystallized at a relatively low temperature.
(iii) host materials have a relatively small composition ratio of anion to cation.

In the requirement i), it is needed that nanocrystals phase-separate with hosts and dopants while forming solid solutions between hosts and dopants. Solubility limit of dopants depends on annealing temperatures and deposition techniques. Carrier concentrations of doped hosts can be controlled by employing different chip numbers and areas of dopants set on sputtering target. In the requirement ii), host materials should be crystallized at relatively low temperatures, since sublimations and partial decomposition of nanocrystalline compounds depend on crystallization temperatures of hosts. In addition, well crystallized hosts are needed to dope with impurities. For instance, crystallization temperature of ZnO host is 623 K (Fig. 4) that is 100 K lower than that using TiO₂ host. In fact, the electrical resistivity (Fig. 10) reduced significantly at temperatures exceeding 623 K, well corresponding to the crystallization temperature of ZnO (Fig. 4). In contrast, Nb- or W-added TiO₂ thin films didn’t exhibit obvious decrease in electrical resistivity in our preliminary experiment within annealing temperatures up to 873 K, because their crystallinities are relatively low. In the requirement iii), productions of undesirable phases (i.e., In₂O₃ and Sb₂O₅, et al.) (Fig. 6) depends on composition ratios of anion to cation in host materials. Specifically, the partially decomposed indium and antimony are often oxidized during heat treatment, since the composites contains excess oxygen from stoichiometric composition of ZnO (Fig. 6) and TiO₂.⁴ Providing a relatively small ratio reasonably decreases an inclusion of oxygen. In fact, crystalline composites using ZnO host contains oxygen concentrations of 50 at.% or less (Fig. 6) in contrast to approximately 60 at.% using TiO₂ host.¹ The reduced oxygen was resulted in no inclusion of the undesirable phases (Fig. 6), although TiO₂ host usually produced those.² Hence, further small ratios (e.g., Cu₂O) might enlarge the composition ranges without such inclusions. If we carefully select materials for nanocrystals, hosts, and dopants following the requirements, one step synthesis would provide the functionalities (i.e., optical absorption shifts and relatively low electrical resistivity) on different composites.

IV. CONCLUSION

We have investigated one-step synthesis of the nanocomposite thin films with InSb nanocrystals embedded in ZnO host doped with Ge. The solubility limit of Ge in ZnO is 2 at.% in the present technique (i.e., sputtering and subsequent heat-treatment at 873 K). The compositional optimization produces the composite containing InSb and ZnO without any undesirable phases (e.g., Sb and In₂O₃). The electrical resistivity of the composite was reduced to 6.6 × 10⁻³ Ω cm at an annealing temperature of 773 K due to a formation of Ge₃Zn₁ₓO solid solution. Simultaneous addition of InSb and Ge to ZnO thin films provides the different functionalities of shifting optical absorption edge in InSb nanocrystals phase-separating with ZnO and of reducing electrical resistivity in dopant Ge forming a solid solution with ZnO.

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