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Creation of Transparent Conducting Amorphous Oxides by Ion Implantation

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Three series of transparent amorphous oxide films composed of p-block cations, xCdO-(100-x)GeO_2, yIn_2O_3-(100-y) Sb_2O_x and zZnO-(100-z)GeO_2, were deposited on SiO_2 glass substrates by rf sputtering method, and doping of proton was performed by ion implantation to generate carrier electrons. Dc conductivities of all as-sputtered films were < 10^{-9} Scm^{-1}. Upon the implantation of protons, the conductivities of the films, of which composition of 78CdO-22GeO_2 and 72In_2O_3-28Sb_2O_x, were enhanced to 210 Scm^{-1} and 1.5×10^{-5} Scm^{-1}, respectively, while those of other films remained to be < 10^{-9} Scm^{-1}.

1. Introduction

Amorphous semiconductors have been classified into three categories such as amorphous chalcogenides (a-chal), hydrogenated silicon (a-Si:H) and oxide glasses containing a large amount of 3d-mixed valence cations.[1~3] Generally mobility of electrons or holes in the amorphous phases is at least one order of magnitude smaller than that of the corresponding crystalline materials. In the case of a-chal and the amorphous oxides, it is difficult to generate electronic carriers by the conventional doping process. Optically these materials are not transparent in visible region. Amorphous materials with high transparency and electrical conductivity have the potential applications in the opto-electronic devices such as the transparent electrodes for LCDs or solar cells.

We have proposed a working hypothesis for searching new transparent conductors and found several new conductive oxides such as $MgIn_2O_4$ or $ZnGa_2O_4$.[4,5] The working hypothesis is that oxides composed of heavy metal cations with an electronic configuration of $(n-1)d^{10}ns^0$ (p-block cations) are promising as mother materials of transparent conductors. This can be applied also to amorphous transparent conductors, and a-$AgSbO_3$, a-Cd_2PbO_x and a-Cd_2GeO_4 were successfully found amorphous.[6~8] It is noteworthy that the mobility of the materials is comparable with that of the crystalline ones, and moreover the electronic carriers were generated in these amorphous specimens by oxygen vacancies or the cation implantation.

In this study, three series of oxide systems composed of p-block cations were chosen so as to obtain the amorphous thin films of high conductivity and wide optical band gap, i.e., xCdO-(100-x)GeO_2, yIn_2O_3-(100-y) Sb_2O_x and zZnO-(100-z)GeO_2. Amorphous nature of these films were confirmed by XRD and electron diffraction pattern. Electrical and optical properties of the as-sputtered and the as-H^+-implanted films were examined.

2. Experimental

Thin films with the chemical composition of xCdO-(100-x)GeO_2, 20<x<80; yIn_2O_3-(100-y)Sb_2O_x, 20<y<75; and zZnO-(100-z)GeO_2, 40<z<70 were deposited on SiO_2 glass substrates by rf sputtering method under the following conditions: rf power, 180 W; sputtering gas, 80%Ar+20%O_2; sputtering pressure, 0.1 Torr; no substrate heating. Thickness (d) of all films estimated to be 500~800 nm by the apparatus of the stylus type. Protons were implanted at room temperature in two steps, 80 kV-5×10^{15} cm^{-2} + 140 kV-5×10^{15} cm^{-2} in the form of H^{2+} ions. These acceleration voltages were selected on the basis of the TRIM calculation to avoid too high local concentration of the implanted protons.[9] Dose rate was ~0.006 μ A cm^{-2} and

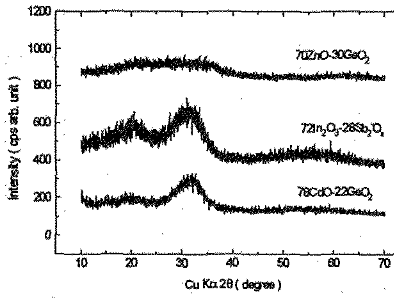

Fig. 1 Glancing angle x-ray diffraction patterns of thin films. Incident angle : 0.5°

total fluence (C) was 2×10^{16} cm^{-2} as H^+ ions.

The amorphous nature of the resulting thin films was confirmed by glancing angle powder XRD and the cross-sectional TEM. Optical absorption spectra were measured using a spectrometer in the wavelength range of 200 nm ~ 2600 nm. Dc conductivity and the Hall effect of these films were measured by the two probe configuration method and the Van der Pauw method as a function of temperature. The chemical compositions of the films were determined by ICP photo-emission spectroscopy for the nitric acid solution.

3. Results

Figure 1 shows the glancing angle XRD patterns of resulting films. These are the typical representative patterns. All patterns of films prepared here indicated only broad peaks. From the observation it can be said that the thin films are in amorphous state judged from XRD. Figure 2 shows the cross-sectional TEM photo of the film with the chemical composition $78CdO$-$22GeO_2$ and the selected area electron diffraction pattern. Since no distinct spot resolved in the diffraction pattern, the films were suggested to be in amorphous state from the order of electron microscopic observation. Figure 3 shows the Tauc plots of the optical absorption of the as-sputtered films and the transmission spectra of films. The Optical band gaps (E_g^{opt}) obtained from the Tauc plot were 3.1~4.4 eV in CdO-GeO_2 films, 2.9~3.0 eV in In_2O_3-Sb_2O_x films and 4.0~4.6 eV in ZnO-GeO_2 films. All films prepared were transparent in visible region. The conductivities of all films before

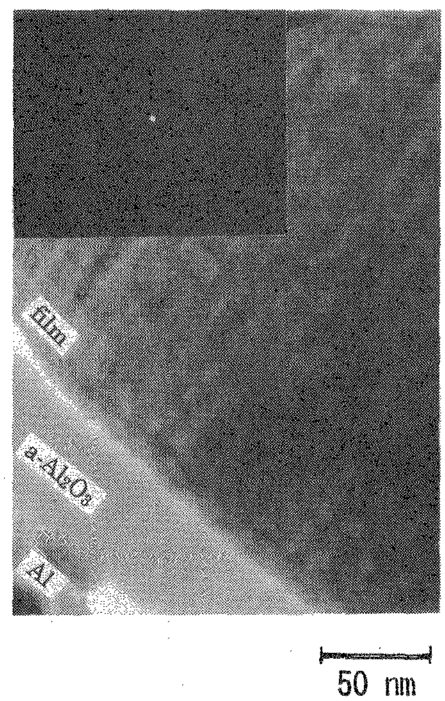

Fig2 Cross-sectional TEM photo and selected area electron diffraction pattern of $78CdO$-$22GeO_2$ film.

the implantation were less than $\sim10^{-9}$ Scm^{-1}. Upon the implantation of protons to a fluence of 2×10^{16} cm^{-2}, the conductivities of the films increased to 210 Scm^{-1} in $78CdO$-$22GeO_2$ film and 1.5×10^{-5} Scm^{-2} in $72In_2O_3$-$28Sb_2O_x$ film, while those of other films remained to be $\sim10^{-9}$ Scm^{-1}. Since the conductivity of the $72In_2O_3$-$28Sb_2O_x$ film did not change after applying the dc bias for 50 hrs, the possibility of ionic conduction was neglected. Figure 4

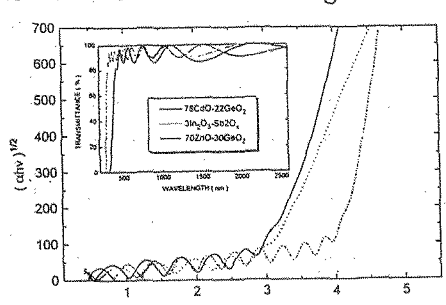

Fig. 3 Tauc plot of optical absorption and optical transmission spectra of amorphous thin films.

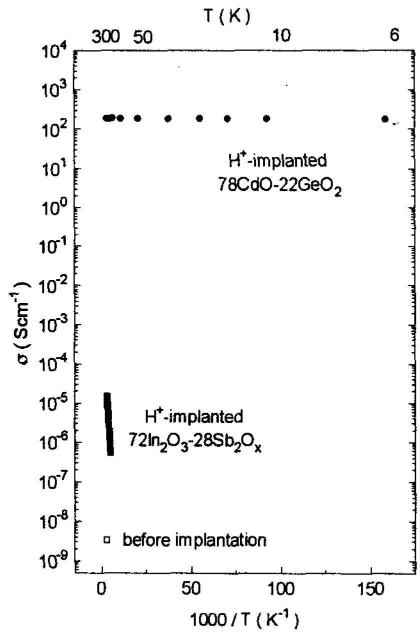

Fig. 4 D.c conductivities of amorphous thin films before and after H^+ implantation as a function of temperature.

shows temperature dependence of the conductivities of films with 78CdO-22GeO_2 and 72In_2O_3-28Sb_2O_x. The conductivity of the film with 78CdO-22GeO_2 remained almost constant down to ~6 K. On the other hand, the conduction of the 72In_2O_3-28Sb_2O_x film was of thermal-activation type and the activation energy calculated from the slope of ln σ versus 1/T plot was ~0.70 eV.

4. Discussion

The mobility of carrier electrons in amorphous 78CdO-22GeO_2 film (μ = ~10 $cm^2V^{-1}s^{-1}$) was extraordinarily large within the existing amorphous film such as a-Si:H or a-chal. Large photocurrent , which is a measure of the extension of conduction band in the specimens, was observed in some films, e.g. xCdO-(100-x)GeO_2, x>70; yIn_2O_3-(100-y)Sb_2O_x, 20<y<75; and zZnO-(100-z)GeO_2, x>70. The facts suggest that our working hypothesis is effective in searching for amorphous electrical conductors.

On the other hand, the carrier generation is also important factor for obtaining the amorphous electrical conductors with high σ. The carrier density (N) of 78CdO-22GeO_2 film was ~ 1×10^{20} cm^{-3} and the carrier generation efficiency (η =Nd/C) of it was ~30%. It is difficult to enhance the electrical conductivity over several orders in the most of amorphous specimen by the doping of impurities except for a-Si:H[1)]. However carrier electrons effectively generated in 78CdO-22GeO_2 film and the conductivity of this film drastically increased by 11 orders of magnitude over the conductivity of the as-sputtered film. Furthermore, since the conductivities remained to be almost constant down to ~6 K, the Fermi level in H^+-implanted film of amorphous cadmium germanate was above the bottom of the conduction band. On the other hand, the conductivity of 72In_2O_3-28Sb_2O_x film was relatively low compared with 78CdO-22GeO_2 film despite the same total fluence of protons. The Hall measurements of these film was unsuccessful, because of high resistivity. Since the photocurrent was observed in these films, the low conductivity of H^+-implanted films must be due to low carrier density. Certain electron trapped centers may exist, e.g. 1) $Sb^{5+}+e^-$ -->Sb^{4+} and 2) H^++e^--->H.[10)] The direct evidence of the difference for carrier generation in amorphous specimen is not obtained so far.

5. Conclusion

Thin films of transparent amorphous oxides in the systems, xCdO-(100-x)GeO_2, yIn_2O_3-(100-y) Sb_2O_x and zZnO-(100-z)GeO_2 were prepared by rf sputtering method. Electrical and optical properties of as H^+-implanted film were examined. Dc conductivities of all as-sputtered films were < 10^{-9} Scm^{-1}, carrier electrons were successfully generated in amorphous film with the composition of 78CdO-22GeO_2 and 72In_2O_3-28Sb_2O_x by the ion implantation. The conductivity of 78CdO-22GeO_2 film was drastically increased to 210 Scm^{-1} by the 11 orders of magnitude. The carrier density and the Hall mobility of this film were 1×10^{20} cm^{-2} and ~10 $cm^2V^{-1}s^{-1}$, respectively. On the other hand, the conductivity of the as-implanted film with the composition of $72In_2O_3$-$28Sb_2O_x$ was 1.5×10^{-5} Scm^{-1} and increased by the 4 orders despite the same total fluence of protons. No increase in the conductivity of other films upon the implantation was observed. Further studies of the mechanism of carrier generation is ongoing.

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