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CONDUCTIVITY INCREASE OF AMORPHOUS Si AND Ge BY Mn

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Amorphous Si and Ge are doped with Mn by co-sputtering. The electrical conductivity is increased by as much as a factor of 10^6~10^7 in some cases by the addition of several at.% Mn. The temperature dependence of the conductivity shows the variable range hopping conduction for both samples with and without Mn. The results can be interpreted by the presence of two conduction processes; the variable range hopping through dangling bonds and that through Mn sites.

1. INTRODUCTION

Doping in amorphous semiconductor has received a great interest in recent years. Ovshinsky et al. reported that the electrical conductivity can be increased by many orders of magnitude in a large variety of amorphous semiconductors if they are prepared by co-sputtering with transition elements.[1,2] The mechanism of the increase of the conductivity, however, is not clear. Previously, we studied electrical conduction mechanism in chalcogenide glasses doped with Mn in relation to the ESR study on the role and incorporation scheme of Mn.[3]

In the present work, we investigate the effect of Mn impurity in amorphous Si and Ge. Hauser reported that impurities with deep lying levels in crystalline Ge form localized states near the Fermi level in amorphous Ge, resulting in a rather large increase of the conductivity.[4] On the other hand, Chopra and Nath suggested that impurities with small solubilities in crystalline Ge have large effects on the electrical conduction in amorphous Ge.[5] Since Mn is not only a deep level impurity but also has a small solubility in crystalline Si and Ge,[6] it is expected to have a large effect on the electrical conduction in amorphous Si and Ge, in addition to the advantage of utilizing microscopic information from ESR measurements.

Preliminary results on ESR in amorphous Si and Ge doped with Mn have already been published.[7] In the present work, we focus our attention mainly on the change of the electrical conductivity by the addition of Mn.

2. EXPERIMENTAL METHOD AND RESULTS

Thin(1.4 μm ∿ 5.0 μm) films doped with Mn were prepared by co-sputtering with a Varian FP-21 rf sputtering system. The films were deposited onto glass substrates in 1.5×10^{-1} torr of 99.995 %-pure argon after pumping the system to a base pressure of 6×10^{-7} torr. The target was supplied with 200 W of rf power at 2 kV. Doping was made by putting metallic Mn wafers on the target of Si or Ge. The amount of doped Mn was estimated from a ratio of the surface area of Mn to that of Si (or Ge) on the target electrode by considering sputtering rates of the individual species.

D.c. electrical conductivity was measured in a planar sample geometry with Au electrodes in the temperature range between liquid nitrogen temperature and room temperature. The conductivity σ obeys the Mott relation,[8]

$$\sigma = \sigma_0 \exp\{-(T_0/T)^{1/4}\}, \qquad (1)$$

for all samples both with and without Mn. Typical examples are shown in Fig. 1. In Fig. 2, σ at room temperature versus concentration of Mn is shown in a log-log scale for various series of experiments. In some cases, σ at room temperature is increased by as much as a factor of $10^6 \sim 10^7$.

Optical transmission was measured with a JASCO SS50T spectrophotometer. In Fig. 3, $\sqrt{\alpha\hbar\omega}$ is plotted against the photon energy $\hbar\omega$, where α is the optical absorption coefficient.

3. DISCUSSION

As is evident from Fig. 2 (a), values of σ increase with the increase of Mn content, but such a behavior is not found in the case of amorphous Ge as shown in Fig. 2 (b). When Mn is introduced in amorphous Ge, σ does not increase with the increase of Mn, but it decreases in some cases. This tendency is also found in the case of amorphous Si with low Mn content. These behaviors can be explained if the electrical conduction is assumed to take place via two paths; the variable range hopping through dangling bonds and the conduction through Mn sites. From a previous result of ESR measurements, it is found that the density of dangling bonds decreases with the increase of Mn content.[7] Therefore it is expected that the conduction through dangling bonds decreases with the increase of Mn. The change of the electrical conductivity by the addition of Mn is determined by a competition between these two opposite effects. For undoped samples with a relatively low conductivity (the unpaired electron density is relatively low), the conduction through Mn sites dominates when Mn is introduced and the conductivity increases with the increase of Mn content. On the other hand, for undoped samples with a relative-

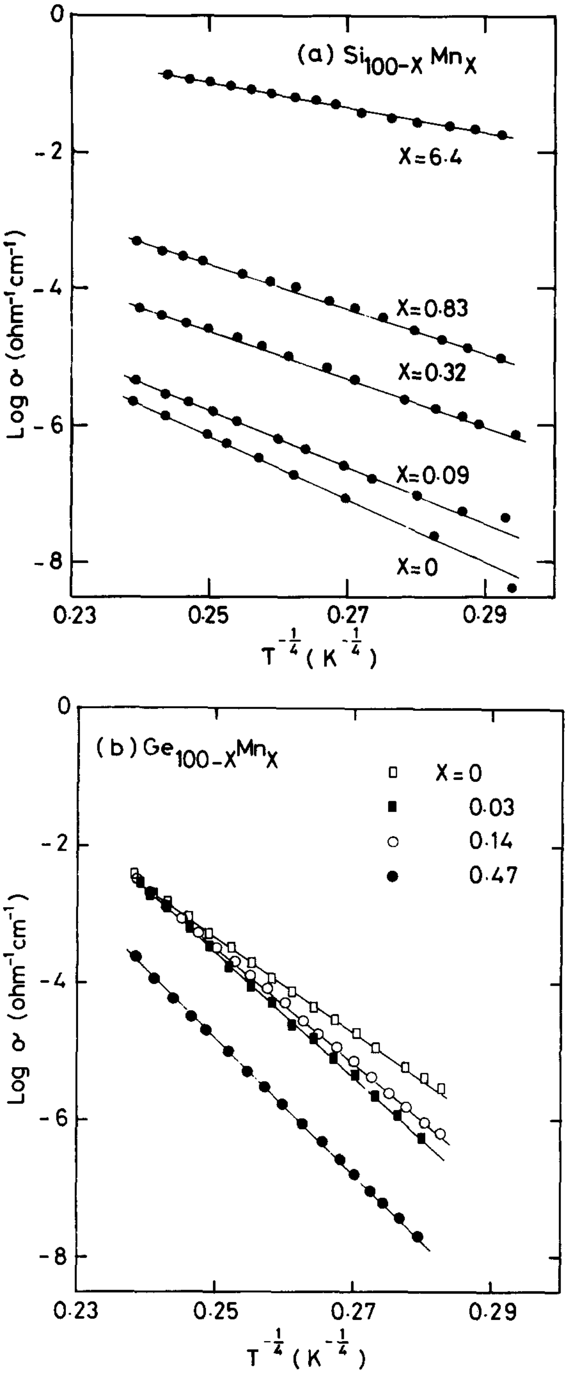

Fig. 1. Temperature dependence of the electrical conductivity σ for $Si_{100-X}Mn_X$ films (a) and $Ge_{100-X}Mn_X$ films (b).

ly high conductivity (the unpaired electron density is high), the conduction through dangling bonds is superior to that through Mn sites up to a critical Mn concentration, and the conductivity remains or decreases with the increase of Mn content.

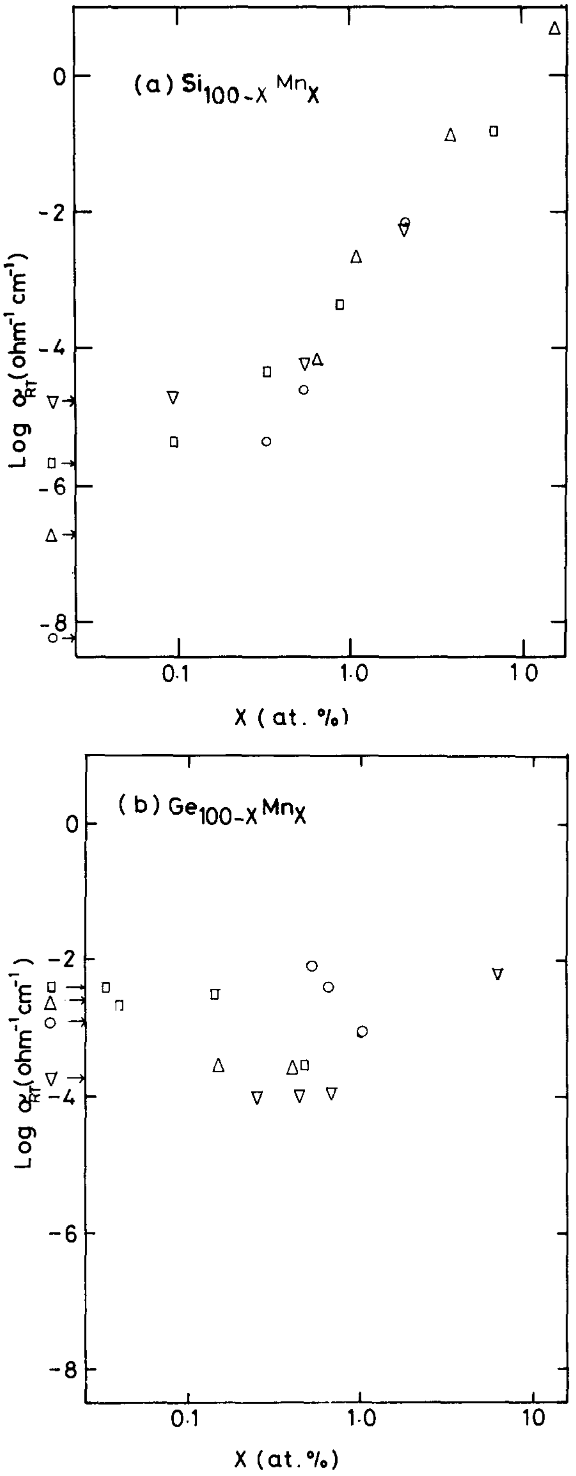

Fig. 2. Dependence of the electrical conductivity at room temperature on Mn concentration for $Si_{100-X}Mn_X$ films (a) and $Ge_{100-X}Mn_X$ films (b). Circles, triangles and squares show the results of different series of experiments. Values of the conductivity for samples without Mn are indicated by arrows.

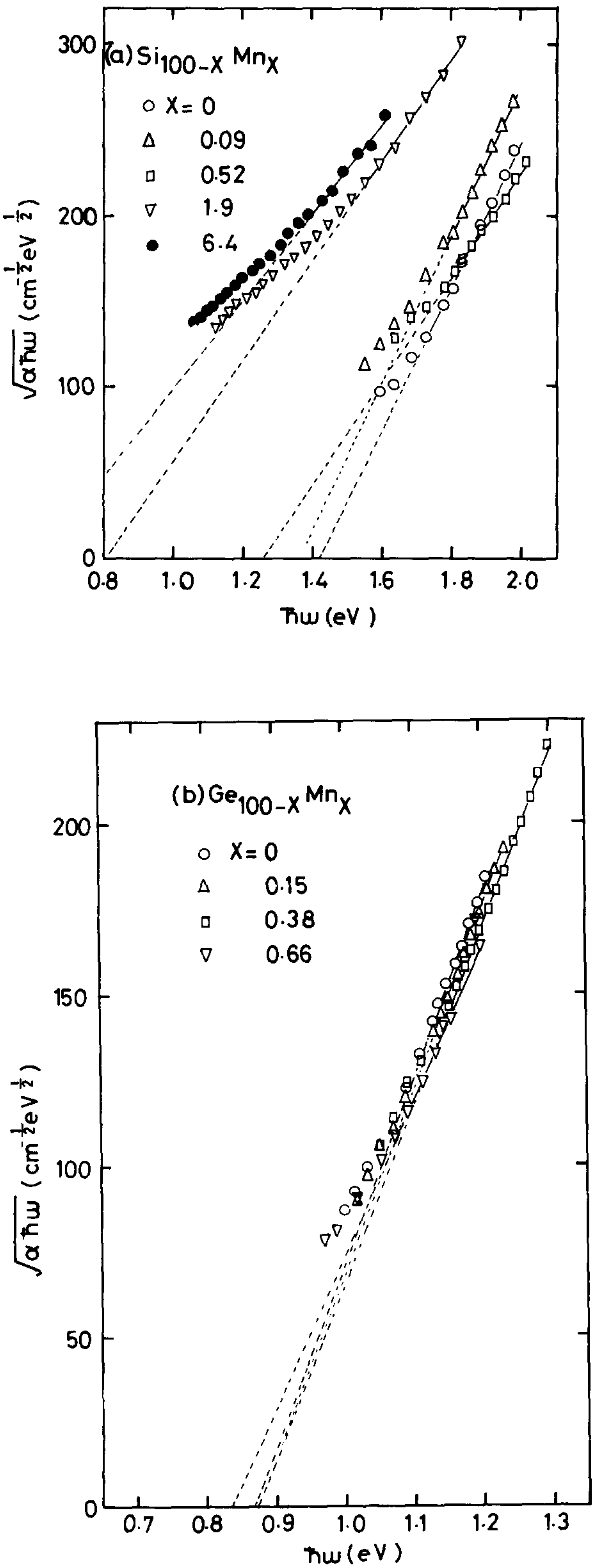

Fig. 3. Dependence of the optical absorption coefficient α at room temperature on the photon energy ħω for $Si_{100-x}Mn_x$ films (a) and $Ge_{100-x}Mn_x$ films (b).

Samples without Mn exhibit some variation in the values of σ in the range between 10^{-8} and 10^{-5} $\Omega^{-1}\text{cm}^{-1}$ for Si and 10^{-4} and 10^{-2} $\Omega^{-1}\text{cm}^{-1}$ for Ge as shown in Fig. 2 (a) and (b). The electrical conductivity of amorphous Si[9,10] and Ge[11] is known to be very sensitive to oxygen during preparation. The presence of oxygen makes the concentration of dangling bonds decrease, resulting in the decrease of the conductivity. In fact, our samples without Mn prepared in 1.5×10^{-1} torr of argon exhibited infrared absorption at 9.5 μm for amorphous Si and 11.5 μm for amorphous Ge, which are ascribed to Si-O and Ge-O vibrations, respectively. But amorphous Si prepared in 5×10^{-2} torr of argon did not exhibit the infrared absorption peak, and had larger conductivity than the samples prepared in 1.5×10^{-1} torr of argon. Therefore, oxygen is considered to be introduced into samples through argon gas. Hence, the scattered values in the conductivity of samples without Mn in Fig. 2 (a) and (b) may be due to oxygen contamination during rf sputtering process.

It should be noticed that the conductivity of amorphous Si with a large amount of Mn is determined by the concentration of Mn irrespective of the magnitude of the conductivity without Mn. Accordingly, the conduction in the case of amorphous Si with a large amount of Mn is considered to take place dominantly through Mn sites. There are not sufficient data for amorphous Ge with the enough amount of Mn to make the conduction through Mn sites dominant, because the samples became crumbly after deposition of Au electrodes by evaporation.

Next problem is the mechanism of the electrical conduction through Mn sites. The temperature dependence of the conductivity obeys Eq. (1) also for samples containing a large amount of Mn, so the conduction is through the variable range hopping. According to the theory of the variable range hopping conduction,[12] T_0 in Eq. (1) is given by

$$T_0 = 16/\{ka^3N(E_F)\}, \qquad (2)$$

where a is the decay length of the localized wave function, k the Boltzmann constant and $N(E_F)$ the density of localized states at the Fermi level. If it is assumed that $N(E_F)$ originates from Mn states and is proportional to the concentration n of Mn such as

$$N(E_F) = b\,n \qquad (3)$$

for samples with a large amount of Mn, Eq. (1) can be written as

$$\sigma = \sigma_0 \exp\{-(n_0/n)^{1/4}\} \qquad (4)$$

with

$$n_0 = 16/(ka^3bT). \qquad (5)$$

Figure 4 shows a log σ versus $n^{-1/4}$ plot for amorphous Si at room temperature. The curve fits a straight line whose slope gives a value of $a^3b = 1.9 \times 10^{-23}$ $\text{cm}^3\text{eV}^{-1}$. If a is assumed to be 2 Å, b^{-1} becomes 0.43 eV, which does not seem an unreasonable value, because b^{-1} corresponds to the energy width of the Mn states.

ESR study shows that Mn is incorporated in amorphous structure in several forms. At present, it is not clear which forms of Mn contribute to $N(E_F)$. If Mn contributing to

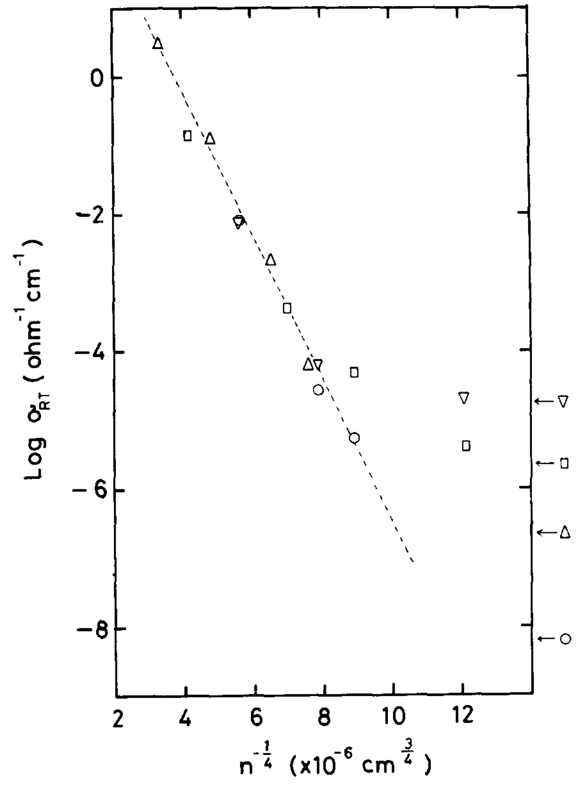

Fig. 4. Dependence of the electrical conductivity σ at room temperature on Mn concentration n for $Si_{100-x}Mn_x$ films. Data in Fig. 2 (a) are replotted in a scale of log σ versus $n^{-1/4}$. Values of σ for samples without Mn are indicated by arrows.

$N(E_F)$ is a fraction of total Mn, the energy width of the Mn states is smaller than b^{-1}. Kishimoto et al. also explained the conduction in amorphous Si-Au films by the variable range hopping through the Au states in the gap.[13]

Annealing at 300°C for 2 hours makes the conductivity for undoped amorphous Si decrease as much as a factor of 10∿100, but the conductivity for amorphous Si doped with a large amount of Mn (more than 1 at.%) is not largely changed by annealing. A large decrease of the conductivity for undoped samples is attributable to the decrease of dangling bonds by annealing, because the conduction takes place through dangling bonds for undoped samples. A small influence of annealing on the conductivity for samples doped with a large amount of Mn is reasonable because the conduction takes place mainly through Mn sites in this case.

The optical gap is deduced from Fig. 3 as a photon energy at which the extrapolation of the linear portion of $\sqrt{\alpha\hbar\omega}$ versus $\hbar\omega$ plot intersects the $\hbar\omega$ axis. It is shown for amorphous Si in Fig. 5 as a function of Mn content together with that for annealed samples. The decrease of the optical gap for as-deposited samples with the increase of Mn content might be ascribed to a similar reason as in the case of Si-Au system,[14] that is,

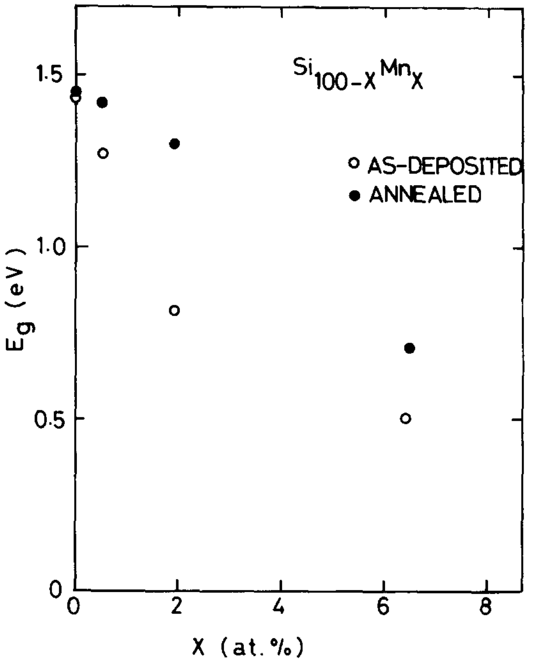

Fig. 5. The optical gap versus Mn concentration for $Si_{100-x}Mn_x$ films. The open circles are for as-deposited samples and the closed ones for samples annealed at 300°C for 2 hours.

Mn states occupy the gap and increase the state density near the band edge. However, it is noticeable that the decrease of the optical gap for annealed samples is smaller than that for as-deposited samples. The increase of the optical gap by annealing is therefore large for amorphous Si doped with Mn, but the increase is very small for undoped samples. The fact also supports the speculation that the conduction takes place not through the band states but the gap states, because the conductivity has no correlation with the optical gap.

In conclusion, Mn has a large effect on the electrical properties of amorphous Si and Ge (especially Si). The conductivity is determined by a competition between the variable range hopping through dangling bonds and that through Mn sites. The latter becomes dominant when the concentration of Mn is large.

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