Solid State Communications, Vol. 23, pp. 833–835, 1977. Pergamon Press. Printed in Great Britain

ELECTRON SPIN RESONANCE IN AMORPHOUS Si AND Ge DOPED WITH Mn

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(*Received* 11 *April* 1977 *by W. Sasaki*)

ESR signal with hyperfine structure due to Mn and that due to dangling bonds are observed. From the magnitude of the hyperfine structure constant, Mn is considered to locate within voids without making a covalent bond with the host atom in the form of Mn^{2+}. The intensity of the ESR signal due to dangling bonds decreases with the increase of that due to Mn, so it is likely that electrons are transfered from Mn to dangling bonds and their unpaired electrons are paired up.

1. INTRODUCTION

DOPING of amorphous Si and Ge (*a*-Si and *a*-Ge) has been of considerable interest in recent years [1–5]. However, there has been no investigation to make clear how impurities are incorporated in the amorphous structure from a microscopic point of view. In the present work, Mn is used as an impurity so as to observe the electron spin resonance (ESR) which is expected to be useful for investigating the microscopic state of the impurity. So far ESR signals due to transition metal ions such as Mn have been reported for various chalcogenide glasses [6–10]. Most of chalcogenide glasses doped with Mn exhibit the signal with $g = 4.3$ having a hyperfine structure, which provides much useful information about the microscopic structure. However, ESR signal due to transition metal ions in amorphous tetrahedral semiconductors has not yet been reported, and to our knowledge, this is a first report on it.

2. EXPERIMENTAL

Samples were prepared by rf sputtering in 1.5×10^{-1} torr of 99.995%-pure argon after pumping the system to a base pressure of 6×10^{-7} torr. 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 by considering sputtering rates of the individual species. The samples were deposited on quartz substrates at rates of 4 Å sec^{-1} (*a*-Si) and 13 $Å^{-1}$ (*a*-Ge). Film thicknesses are 1.5 μm (*a*-Si) and 4.5 μm (*a*-Ge). The ESR measurements were performed mainly at room temperature with a JEOL PE3X spectrometer operating at X-band with 100 kHz modulation. The center density was determined by comparison with a JEOL standard sample. As for Mn signals, the center density was estimated by assuming spin 5/2. The overlapping of the hyperfine lines and also the signal from dangling bonds might make the estimated center density for Mn signals with the hyperfine structure less accurate.

3. RESULTS AND DISCUSSION

For *a*-Si and *a*-Ge doped with Mn, six hyperfine lines with $g = 2.0$ due to Mn are observed besides the signal due to dangling bonds. Typical examples of the signal at room temperature are shown in Fig. 1. At liquid nitrogen temperature, the linewidths of both the hyperfine lines and the dangling bond signals decrease slightly, but the overall shape looks similar to respective ones at room temperature. The center density of the signal due to Mn increases with the increase of Mn content as shown in Fig. 2, but this density appears to be far smaller than the amount of doped Mn, although the amount of doped Mn is not so definite. In addition, the center density becomes smaller by annealing as shown in Fig. 3. These results indicate that there should be at least two ways of incorporation of Mn into *a*-Si or *a*-Ge; Mn contributing to the ESR signal and Mn showing no ESR signal. The observed magnitude of the hyperfine structure constant A is about 95 G for both *a*-Si and *a*-Ge. This magnitude is very close to that for a free Mn^{2+} ion. A is known to decrease largely when Mn makes a covalent bond with surrounding atoms. Therefore, we speculate that the Mn ions locate rather freely within voids in the form of Mn^{2+} ($3d^5$) without making covalent bonds with Si and Ge. The ESR center density of the dangling bonds N_s(D.B.) decreases as that of Mn N_s(Mn) increases as shown in Fig. 2, so it is likely that Mn becomes Mn^{2+} by transfering electrons to dangling bonds and their unpaired electrons are paired up. If this is true, the amount of the decrease of the ESR center density of the dangling bonds ΔN_s(D.B.) is equal to twice the ESR center density of Mn $2N_s$(Mn). Figure 4 shows the log–log plot of ΔN_s(D.B.) vs $2N_s$(Mn). From this figure it can be seen

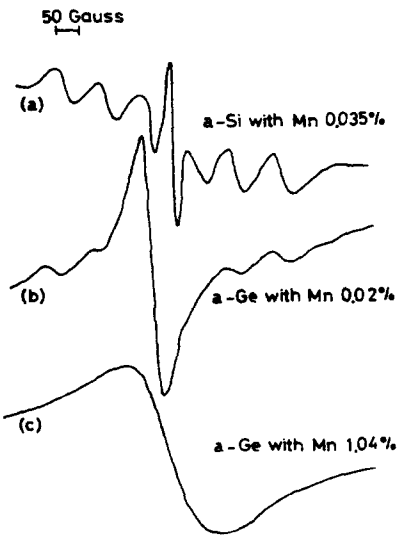

Fig. 1. Typical ESR signals for Mn doped amorphous Si (a) and Ge (b). A signal for Ge with relatively large amount of Mn has no hyperfine structure (c).

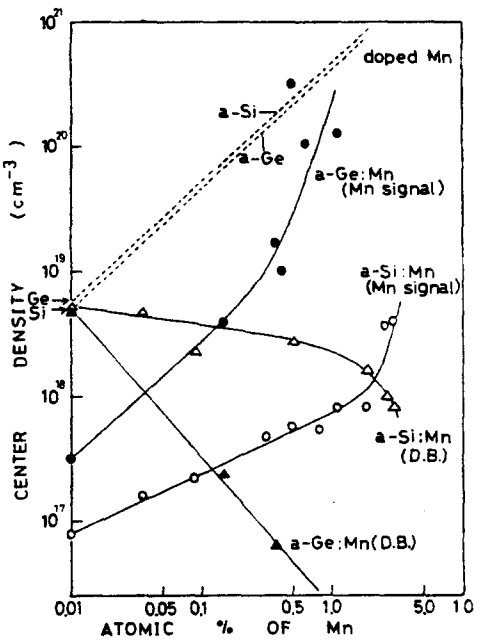

Fig. 2. Dependence of the center density of the ESR signal due to dangling bonds (D.B.) and that due to Mn on Mn content in amorphous Si and Ge. The arrows show the center densities of dangling bonds for samples without Mn. Dashed lines indicate the amounts of doped Mn.

that ΔN_s(D.B.) is close to $2N_s$(Mn). The linewidth of the signal due to dangling bonds is found to increase with Mn content for *a*-Si (7.1 G for 0 at.% Mn and 9.6 G for 1.9 at.% Mn at room temperature). In the case of *a*-Ge, such a change of the linewidth with Mn content

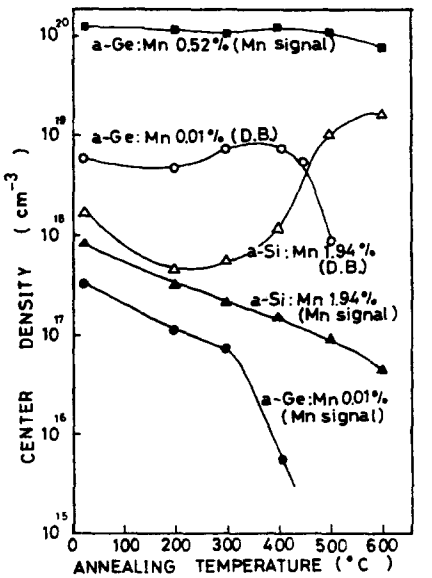

Fig. 3. Annealing temperature dependence of the center density of the ESR signal due to dangling bonds (D.B.) and that due to Mn. Samples are annealed for 30 min.

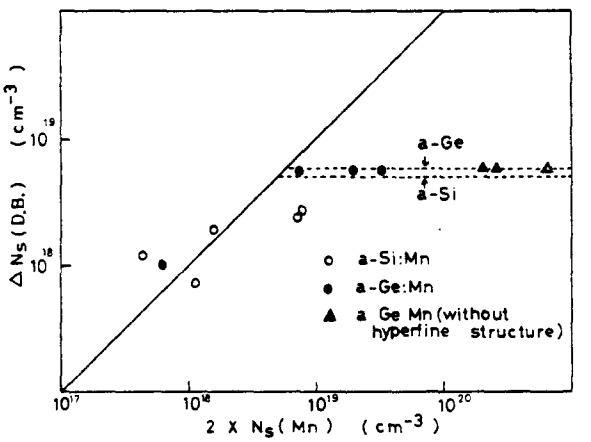

Fig. 4. Decrease of the center density of the ESR signal due to dangling bonds [ΔN_s(D.B.)] vs twice the center density of that due to Mn [$2N_s$(Mn)]. Dashed lines show N_s(D.B.) for samples without Mn.

is difficult to be detected because the signal due to dangling bonds becomes very weak when Mn is doped. When $2N_s$(Mn) is larger than N_s(D.B.), there are not enough dangling bonds to accept electrons from Mn. For *a*-Ge, such a situation occurs above 0.5 at.% Mn content. For *a*-Ge with Mn content larger than 0.5 at.%, the ESR signal is found to change from the six hyperfine lines to a single line as shown in Fig. 1(c). This single line without hyperfine structure has a Lorentzian shape and a linewidth of 220 G at room temperature and is considered to originate from several Mn atoms or ions interacting strongly with each other. It is interesting

that hyperfine structure disappears when $2N_s$(Mn) exceeds N_s(D.B.). For *a*-Si, $2N_s$(Mn) does not exceed N_s(D.B.) (the largest Mn content in our samples was 3.1 at.%), and the signal always shows hyperfine structure. The center density of the signal without hyperfine structure does not change with annealing in contrast to that with hyperfine structure shown in Fig. 3. The incorporation scheme of Mn atoms without showing ESR is not clear at present. It is possible that they are in the form of a phase-separated Mn cluster, an antiferromagnetically coupled Mn^{2+} pair or $Mn^0(3d^7)$ with non-vanishing orbital angular momentum. The changes of electrical and optical properties by doping *a*-Si and *a*-Ge with Mn will be reported elsewhere in connection with the present results of the ESR measurements.

Acknowledgement – The authors wish to thank Dr. M. Suhara for the use of the ESR spectrometer at Faculty of Science of Kanazawa University. Grants from the Nishina Memorial Foundation are gratefully acknowledged.

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