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ESR OF TRANSITION METALS IN a-Si

Tatsuo Shimizu, Minoru Kumeda, Ichiro Watanabe and Yasuhide Noumi

Department of Electronics
Kanazawa University
Kanazawa 920
Japan

Electrical conductivity largely increases and the center density of ESR due to dangling bonds decreases by the addition of transition elements in a-Si. ESR signals due to transition elements are observed at low temperature, the center density of which are largest for about 1 at.% doped samples. In the case of Mn, a signal with hyperfine lines appears. The optical gap decreases with the increase in transition element content. The electrical conduction is suggested to occur mainly by variable range hopping through transition element sites for samples doped with more than 1 at.%.

INTRODUCTION

Controlling the electrical properties of amorphous semiconductors by the addition of different elements has been of considerable interest in recent years. Hydrogenated amorphous silicon (a-Si) was found to be doped with donors or acceptors. Ovshinsky et al. [1] recently reported that the electrical conductivity can be increased by many orders of magnitude in a variety of amorphous semiconductors by the addition of several at.% of transition elements by co-sputtering method. The present authors have already published results of ESR [2], electrical and optical measurements [3] on rf-sputtered a-Si doped with Mn by co-sputtering method. The present work is an extension of the previous studies on a-Si with Mn dopant to other transition element dopants, Fe and Ni. Influence of varying sputtering conditions is also investigated.

EXPERIMENTAL

Sample films were prepared by co-sputtering transition metals with Si with a Varian FP-21 rf-sputtering system. The Ar gas pressure during sputtering was 5×10^{-2} Torr or 1.5×10^{-1} Torr. The ionization gauge for measuring gas pressure is usually calibrated to N_2 gas. The ionization sensitivity of Ar is larger than that of N_2 by about 30 %, but this discrepancy was neglected for measuring Ar gas pressure. Hydrogenated samples were prepared by mixing H_2 gas into Ar gas. The H_2 gas pressure quoted are those corrected by considering the ionization sensitivity. Fused quartz or glass substrates were used for ESR or electrical and optical measurements, respectively. The transition element contents of some of the films were measured by electron probe micro analysis (EPMA). The resuls agree within about a factor of two with those estimated from the ratio of the target areas by taking account of sputtering rates. The latters are used in this paper as transition element contents. Electrical conductivity was measured using Au electrodes in a planar configuration between 140 and 500 K. Samples were previously annealed at 300°C for 2 h for measurements above room temperature in order to avoid annealing effects during the measurement. ESR measurements were performed with a JEOL PE 3X spectrometer between liquid nitrogen temperature and room temperature. The ESR center density was obtained by comparing the absorption area with that of a JEOL standard sample and by assuming spin S = 1/2. Only in the case of ESR signals with

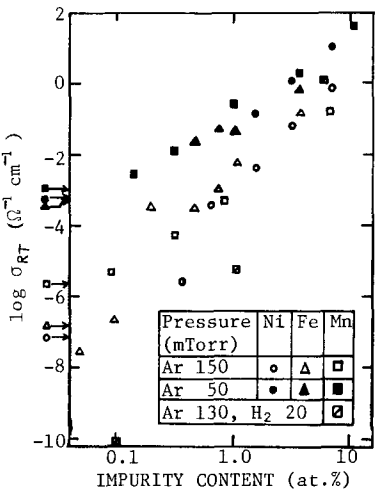

Fig. 1. The electrical conductivity at room temperature σ_{RT} versus transition element content. Arrows at the ordinate show σ_{RT} for samples without transition elements.

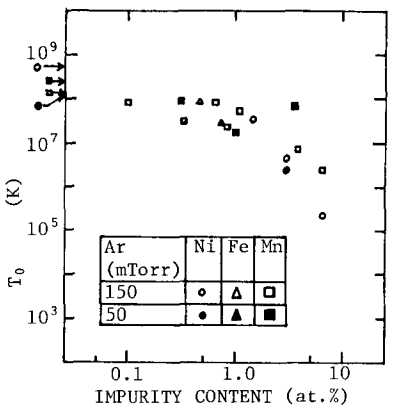

Fig. 2. The slope T_0 of log σ versus $T^{-1/4}$ plot as a function of the transition element content. Arrows at the ordinate show T_0 for samples without transition elements.

hyperfine structure (hfs) from Mn, S was taken as 5/2. Optical absorption coefficient was obtained from transmission and reflection measurements at room temperature.

RESULTS

1. Electrical Conductivity

The electrical conductivity at room temperature σ_{RT} increases with the increase in the transition element content as shown in Fig. 1. σ_{RT} does not depend on the kind of transition elements, but it depends on the Ar gas pressure during sputtering. Although the change of σ_{RT} with the change of the Ar gas pressure is large in the range of small impurity concentration, it is small in the range of large impurity concentration. The effect of hydrogenation is not large for samples doped with transition elements in contrast with the case of shallow impurities. Temperature dependence of the electrical conductivity σ obeys the variable range hopping conduction type,

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

for as-deposited films both with and without transition elements. The constant T_0 decreases with the transition element content as shown in Fig. 2. In the concentration range between 0.5 and 5.0 at.%, T_0 is roughly proportional to the inverse of the transition element content. By annealing the films at 300°C for 2 h, the activation type conduction appears in the high temperature range. The activation energy has a tendency of decreasing with the transition element content.

2. ESR

The center density of the ESR signal due to dangling bonds with g = 2.0055 decreases with the increase in transition element content. The g-value does not change largely but the linewidth tends to increase with the addition of transition elements. Samples added with Mn under 1.5 x 10^{-1} Torr of Ar gas exhibit both at room and liquid nitrogen temperature an ESR signal which has hfs with a hyperfine structure constant of 93 G as already reported previously [3]. At liquid nitrogen

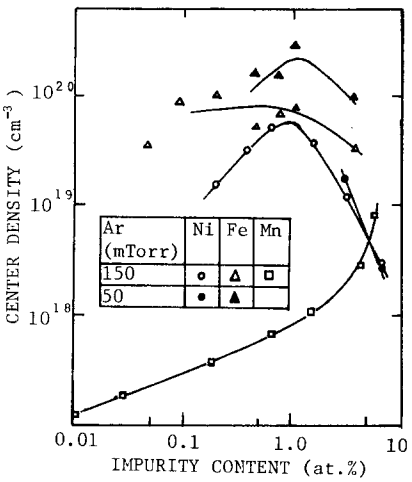

Fig. 3. The center density of ESR due to transition elements versus concentration measured at 77 K.

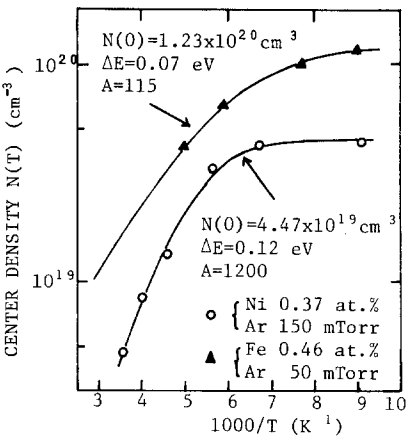

Fig. 4. Temperature dependence of the center density of ESR due to Fe or Ni. Solid curves represent a theoretical expression with suitable parameters as indicated.

temperature, and ESR signal which appears to originate from Fe or Ni is observed for samples added with Fe or Ni, respectively, in addition to the ESR signal due to dangling bonds. The g-values are 2.01 ∿ 2.04 for Fe and 2.01 ∿ 2.015 for Ni. The linewidths are 50 ∿ 90 G for Fe and 30 ∿ 40 G for Ni. These signals do not change largely with Ar gas pressure during sputtering, but the signal with a hfs appears only for the Mn doped sample prepared in high Ar gas pressure. Some samples doped with Mn prepared in 5 x 10^{-2} Torr of Ar gas exhibit a weak broad ESR signal similar to that for Ni doped samples, but its origin is not clear at present. Samples doped with Mn prepared in a mixture of H_2 and Ar gas (a total pressure of 1.5 x 10^{-1} Torr) also exhibit the ESR signal with hfs similar to that for samples without hydrogen. The center density N_S of ESR due to transition element is shown in Fig. 3. as a function of the transition element content. Except for the hfs signal of Mn, N_S increases with the transition element content up to about 1 at.% and then decreases. N_S decreases with raising temperature as shown in Fig. 4 for Fe or Ni doped a-Si, while that of the hfs signal does not change with temperature.

3. Optical Absorption

The plot of $\sqrt{\alpha h\nu}$ versus $h\nu$ became linear for our samples, where α is the optical absorption coefficient and $h\nu$ the photon energy. The extrapolation of this line to $\alpha = 0$ defines the optical gap. The optical gap decreases with the increase in the transition element content as shown in Fig. 5.

4. Thermoelectric Power

The thermoelectric power for annealed samples without transition elements is about -500 μV/deg at 400 K and increases with temperature. The thermoelectric power for samples with transition elements becomes so small that it is difficult to obtain reliable data. The magnitude of the thermoelectric power is within ±20 μV/deg between 300 and 450 K and its sign changes from sample to sample.

5. Annealing Effects

The electrical conductivity at room temperature decreases by annealing at 300°C for 2 h. However, the change is much smaller for samples with transition elements

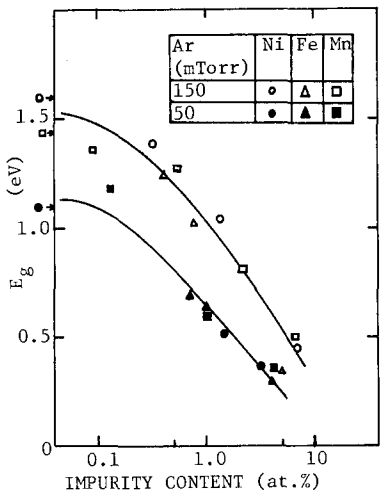

Fig. 5. The optical gap Eg as a function of transition element content.

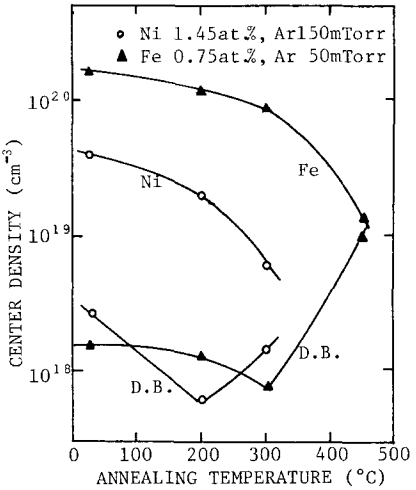

Fig. 6. Changes with annealing at 300°C for 2 h of the center densities of ESR due to dangling bonds (D.B.) and transition elements.

than for samples without them. Both the center densities of the ESR signals due to dangling bonds and transition elements change by annealing as shown in Fig. 6. The center density of ESR due to dangling bonds decreases, reaches a minimum and then increases with the increase of annealing temperature. The center density of ESR due to transition elements decreases by annealing. The optical gap increases by annealing by 0.1 ∿ 0.4 eV.

DISCUSSION

Temperature dependence of the electrical conductivity for samples added with transition metal elements shows that the electrical conduction takes place mainly by variable range hopping. The increase in transition element content decreases the center density of ESR due to dangling bonds and increases the conductivity. It is noticeable that the electrical conductivity is almost the same for samples added with Mn, Fe and Ni. From these results, it is suggested that the variable range hopping conduction takes place through the site of transition elements as was already reported in detail for Mn doped a-Si [3]. T_0 in eq. (1) is considered to be inversely proportional to the transition element content in this case. The proportionality is roughly recognized in Fig. 2 between 0.5 and 5 at.% of transition element content. Alzamir et al. reported that T_0 changes exponentially with the transition element content [4]. Because of a rather large scattering of the data, it is rather difficult to distinguish between the linear and the exponential dependence of T_0 on the impurity content.

ESR signals from transition elements were detected for the first time at low temperature for tetrahedrally bonded amorphous semiconductors except for the ESR signals with a hfs from Mn reported by the present authors [2]. Details of the hfs lines were already reported, so that it will not be repeated here. The reason why the ESR due to Mn changes with Ar gas pressure is not clear at present, but it is known that properties of Si films largely depend on Ar gas pressure [5]. The film prepared in high Ar gas pressure has a low concentration of the ESR center due to dangling bonds and a small electrical conductivity. Further it contains oxygen

and less Ar. The center density for the ESR signal due to Fe or Ni has a peculiar dependence on the transition element content and decreases with the increase of temperature as shown in Fig. 3 and 4, respectively. So far, it has been believed that no ESR signal from Fe appears in tetrahedrally bonded amorphous semiconductor films [6] when Fe content is not so large as to make these films ferromagnetic. It should be noticed that only some fraction of incorporated transition elements contributes to ESR. The center density of ESR due to transition elements decreases with the increase in the transition element content above about 1 at.%, but the electrical conductivity continues to increase with it. Accordingly, transition element atoms contributing to the electrical conduction is considered to be different from those contributing to ESR.

Annealing the samples above 200 ∿ 300°C makes the center density of ESR due to transition elements smaller and that due to dangling bonds larger as shown in Fig. 6. The electrical conductivity has a tendency of the decrease with annealing at 300°C. These facts suggest that some fraction of transition element atoms become clustered by annealing and an effective content of them becomes smaller because the clustered atoms contribute to neither the electrical conduction nor the ESR. The temperature dependence of ESR due to transition elements can be explained as follows. It is assumed that the ground state contributes to the ESR and there exists an excited state which is separated by ΔE from the ground state and does not contribute to the ESR. Then the ESR center density as a function of temperature N(T) becomes

$$N(T) = N(0)\{1 + A \exp(-\Delta E/kT)\}^{-1}, \qquad (2)$$

where A is a ratio of the degeneracy of the excited state to that of the ground state. By fitting this expression to the observed temperature dependence, values of N(0), A and ΔE can be obtained. These values are shown in Fig. 6 and the calculated curves are shown by solid lines. Similar behaviors were reported for interstitial Fe in crystalline Si [7]. In that case, the ground state is $Fe^0(3d^8)$ and the excited states are $3d^7$.

A peculiar dependence of the ESR center density on transition element content may also be explained by assuming that the electronic configuration of transition element changes by the shift of the Fermi level caused by the increase in the transition element content. ESR center density decreases with the increase in the transition element content if the Fermi level shift makes the electronic configuration change to the configuration which does not exhibit ESR. Thermoelectric power becomes very small by the addition of transition elements, so it is difficult to deduce from its sign the direction of the Fermi level shift because it appears that the thermoelectric power is not determined by the extended state conduction but by the variable range hopping conduction through the site of transition elements. As seen from Fig. 5, the optical gap decreases rather largely with the addition of transition elements. The electrical conduction takes place mainly by the variable range hopping conduction, so it is rather difficult to obtain a reliable value of the activation energy for the conduction in band states even for the annealed samples. However, it appears that the activation energy decreases with transition element content. The decrease in the optical gap is not so different from that of twice the activation energy. Accordingly, the shift of the Fermi level appears to be not so large even if it exists. In the case of Au, a rather large shift of the Fermi level has been observed [8]. The difference between the two cases can be explained by noticing that the impurity level locates near the center of the gap for transition elements, while it locates rather close to the valence band edge for Au.

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