

## Electron spin resonance study of platinum-manganese complexes in Si

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### Abstract

We have investigated platinum-manganese complex in silicon by electron spin resonance (ESR) measurement. The ESR signals originating from a platinum-manganese complex have been observed in both of n-type and p-type Si. The anisotropic g-tensor obtained by analyzing the angular dependence of the ESR signals indicated the trigonal ( $C_{3v}$ ) symmetry with the g-values of  $g_{\parallel} = 2.2$ ,  $g_{\perp} = 2.1$ , and the  $g_{\parallel}$  axis along  $\langle 111 \rangle$  direction. It was expected that the complex consisted of a substitutional platinum and an interstitial manganese. We also studied a dissociation of platinum-manganese complex by thermal treatment from 380°C to 450°C. The activation energy for the dissociation of platinum-manganese complex was determined to be about 0.96 eV. The activation energy approximated to the activation energy for the diffusion of interstitial manganese in Si. These results suggested that the Pt-Mn complex was dissociated by the removal of Mn atom from an interstitial site neighboring on a substitutional Pt atom.

### 1. Introduction

Transition-metal impurities produce energy levels in the bandgap of silicon. Such defects are much important in understanding of the electrical properties of Si. The defect structures and the electronic levels of transition-metal impurities in Si have been studied widely by measurements of electron spin resonance (ESR) and deep-level transient spectroscopy (DLTS). In particular, the valuable information on the defect structure can be obtained by ESR measurement. The structures and properties of transition-metal impurities in Si have been investigated intensively using the ESR method [1]. In addition to the isolated transition-metal impurities, the complexes involving transition-metal impurities have deserved particular attention. The defect structures, the electronic levels, and the thermal stabilities of the transition-metal complexes has been much interested.

Recently, the properties of platinum-related defects in Si have been extensively studied, because Pt is used as a lifetime controller in such devices as fast switching diode and thyristor. The defect structures, the electronic levels, and the local vibrational modes of various Pt-related defects, such as isolated Pt, Pt-Pt pair, and Pt-hydrogen complexes, have been identified by measurements of ESR [2-9], DLTS [10-12], and optical-absorption spectra [7, 11, 13]. On the other hand, manganese is also an important representative of transition-metal impurities in Si. Manganese in Si forms a large variety of isolated interstitial defects like  $Mn^{2+}_i$ ,  $Mn^{+}_i$ ,  $Mn^0_i$ , and substitutional  $Mn^{+}_s$ ,  $Mn^{2-}_s$  [1,14], in addition to the complexes with other impurities, such as acceptor atoms. However, the complexes consisting of two transition-metal atoms have been little investigated. Although the symmetries of the complexes are expected by ESR measurements [1], the thermal stabilities have been unclear. The ESR of Pt-Mn complex has been reported by Woodbury and Ludwig [1]. The anisotropic g-tensor of Pt-Mn complex indicated the trigonal ( $C_{3v}$ ) symmetry with the g-values of  $g_{\parallel} = 2.027$ ,  $g_{\perp} = 2.017$ . It has been well known that isolated Pt atom is occupied on a substitutional site distorted off center in a  $\langle 100 \rangle$  direction and isolated Mn atom on an interstitial site in Si. Therefore, it has been expected that the Pt-Mn complex with the trigonal ( $C_{3v}$ ) symmetry

consists of a substitutional Pt atom and an interstitial Mn atom.

In this paper, we report on the thermal stability of Pt-Mn complex in Si investigated by ESR measurements. We observed the ESR signals of Pt-Mn complex in both of n-type and p-type Si. The anisotropic g-values of the Pt-Mn complex were  $g_{\parallel} = 2.2$ ,  $g_{\perp} = 2.1$ , and they also indicated the trigonal ( $C_{3v}$ ) symmetry. The hyperfine structure showed that the ESR signal was related to a Pt atom and a Mn atom. Typically, an isolated Pt and Mn occupied on a substitutional and an interstitial site in Si, respectively. It was expected that the Pt-Mn complex with the trigonal ( $C_{3v}$ ) symmetry consisted of a substitutional Pt and an interstitial Mn. It is thought that the observed ESR signals are due to the same Pt-Mn complex that had been already reported [1] although there is only a little difference between both g-values. In addition, we investigated the dissociation of the Pt-Mn complex by thermal treatment. The activation energy for the dissociation of Pt-Mn complex was determined to be about 0.96 eV, which was a little higher than the activation energy for the diffusion of interstitial Mn in Si [15]. It was probable that the Pt-Mn complex was dissociated by the removal of Mn atom from an interstitial site neighboring on a substitutional Pt atom.

## 2. Experimental Procedures

The samples used in this study were prepared from (001)-oriented Czochralski (CZ) and float zone (FZ) Si. Starting resistivities of the samples were  $17 \Omega \cdot \text{cm}$  for B-doped and  $12 \Omega \cdot \text{cm}$  for P-doped CZ Si, respectively, and was  $10 \Omega \cdot \text{cm}$  for P-doped FZ Si. The samples were cut from the crystals into bar-shaped samples with typical dimensions of  $2 \times 3 \times 15 \text{ mm}^3$  and with the longest side parallel to the  $[110]$ . Platinum was evaporated on one side of samples. The samples covered with Pt were sealed in quartz capsules with Ar gas at 0.2 atm and annealed at  $1250^\circ\text{C}$  for 24 h followed by quenching in water. The residual Pt was removed from the surfaces of samples by etching in mixed acid. Subsequently, the Pt-doped samples sealed with a piece of Mn and Ar gas at 0.2 atm in a quartz capsules were annealed at  $1100^\circ\text{C}$  for 6 h, and then quenched in water. The samples doped with Pt and Mn were annealed from  $380^\circ\text{C}$  to  $450^\circ\text{C}$  in Ar atmosphere followed by quenching in liquid nitrogen to investigate the dissociation of Pt-Mn complex. The ESR measurements were performed at 8 K with an X-band ( $\nu \approx 8.9 \text{ GHz}$ ) spectrometer and a cylindrical microwave cavity of  $\text{TE}_{011}$  mode, using a lock-in amplifier and magnetic modulation with a frequency of 100 kHz.

## 3. Experimental Results and Discussion

The ESR signals of  $\text{Pt}_s^-$  in the n-type sample doped with Pt,  $\text{Mn}_i^0$  in the p-type sample doped with Mn, and Pt-Mn complex in the p-type sample doped with Pt and Mn are shown in Fig. 1 (a), (b), and (c), respectively. The ESR measurements is performed at 8 K under magnetic field parallel to the  $[001]$  direction. The each ESR signal in Fig. 1 is observed in both of CZ and FZ samples. The ESR signals of isolated  $\text{Pt}_s^-$  in the n-type sample doped with Pt are observed around 310 mT. They are composed of a center line and two satellite lines due to  $^{195}\text{Pt}$  isotope with nuclear spin  $I = 1/2$  and natural abundance 33.8%.

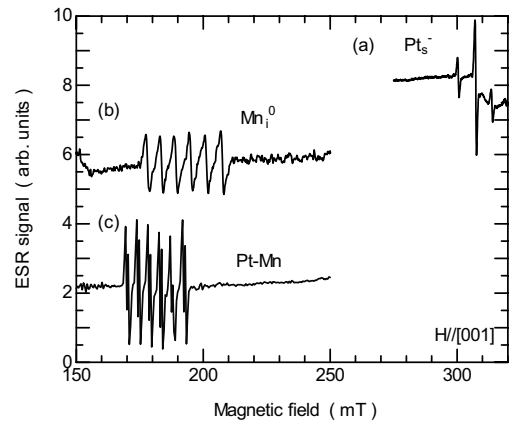


FIG. 1: ESR signals of (a)  $\text{Pt}_s^-$  in the n-type sample doped with Pt, (b)  $\text{Mn}_i^0$  in the p-type sample doped with Mn, and (c) Pt-Mn complex in the p-type sample doped with Pt and Mn at 8 K. The magnetic field is parallel to  $[001]$  direction. The microwave frequency is about 8.9 GHz.

The anisotropic  $g$ -values of  $g_{[110]} = 1.346$ ,  $g_{[-110]} = 1.419$ , and  $g_{[001]} = 2.096$  for  $\text{Pt}_s^-$  obtained in this study are comparable to previously reported  $g$ -values [2, 4]. The isolated  $\text{Pt}_s^-$  is in orthorhombic ( $C_{2v}$ ) symmetry because of the distortion of the off Pt center in a  $\langle 100 \rangle$  direction. On the other hand, the signals of  $\text{Mn}_i^0$  in the p-type sample doped with Mn are shown in Fig. 1 (b). The sixfold hyperfine splitting due to  $^{55}\text{Mn}$  with nuclear spin  $I = 5/2$  and natural abundance 100% are observed. The isotropic  $g$ -value of 3.324 is comparable to previously reported  $g$ -values of  $\text{Mn}_i^0$  [1]. In the p-type sample doped with Pt and Mn, ESR signals are detected around 180 mT under magnetic field parallel to [001] direction, as shown in Fig. 1 (c). The signals in Fig. 1 (c) are also observed in both of n-type and p-type samples. The ESR signals of  $\text{Mn}_i^0$  is not observed in the samples doped with Pt and Mn. Moreover, the ESR signals of isolated  $\text{Pt}_s^-$  can be detected a little in the sample doped with Pt and Mn only under illumination. These mean that most of Pt and Mn atoms are present in the form of the complex in this sample.

Figure 2 shows the hyperfine structure of the signals in the p-type sample doped with Pt and Mn. The six equivalent components are indicated by dotted arrows. The sixfold splittings are due to the hyperfine interaction with one Mn atom. Furthermore, the one component is composed of a center line and two satellite lines with a ratio of intensities near to 1:4:1, as indicated by solid arrows in Fig. 2. The hyperfine splitting is related to one Pt atom. The hyperfine structure in Fig. 2 proves that the ESR signals are originated from a defects containing one Pt and one Mn atoms. The ESR signals of Pt-Mn complex in Fig. 1 (c) are anisotropic. Three groups of the signals with the hyperfine structure in Fig. 2 are observed when the magnetic field is rotated in (110) plane from [001] direction to [110] direction. Experimental and fitted angular dependence of the  $g$ -values at central magnetic fields of the hyperfine structures are shown in Fig. 3. The spin state of Pt-Mn complex in Si is  $S = 3/2$  and the fine structure is in case of larger  $D$  ( $|2D| \gg h\nu$ ) [1]. The angular dependence of the  $g$ -values is fitted with effective spin Hamiltonian for Kramers doublet which has an effective spin and effective  $g$ -values give by  $S' = 1/2$ ,  $g'_\parallel = g_\parallel$ ,  $g'_\perp = g_\perp(S+1/2)$ . The calculated  $g$ -values are  $g_\parallel = 2.2$ ,  $g_\perp = 2.1$ , which correspond to those reported by Woodbury and Ludwig [1], and the  $g_\parallel$  axis is along  $\langle 111 \rangle$  direction. These indicate that Pt-Mn complex is in the trigonal ( $C_{3v}$ ) symmetry. In the case of isolated defect, Pt and Mn atoms occupy a substitutional site and an interstitial site in Si, respectively. Therefore, it can be simply expected that the complex with the trigonal ( $C_{3v}$ ) symmetry

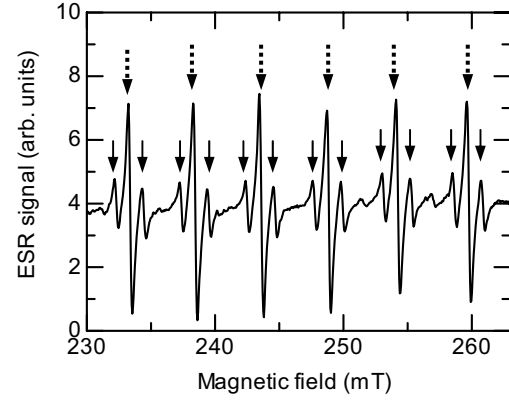


FIG. 2: The hyperfine structure of the ESR signals in the p-type sample doped with Pt and Mn at 8 K. The magnetic field is near to [110] direction. The hyperfine splittings due to  $^{195}\text{Pt}$  and  $^{55}\text{Mn}$  are indicated by solid arrows and dotted arrows, respectively.

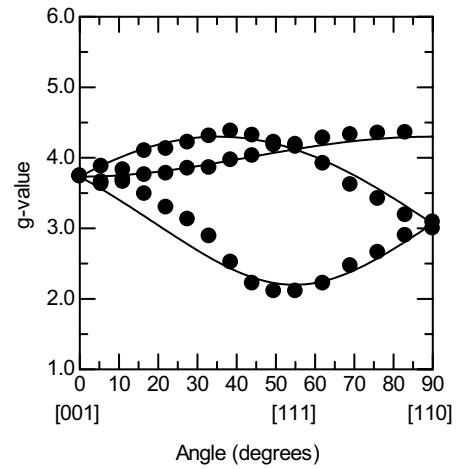


FIG. 3: Angular dependence of the  $g$ -values at the central magnetic fields of the hyperfine structures for the Pt-Mn complex. Calculated curves are also indicated by solid lines. The magnetic field is rotated in (110) plane from [001] direction to [110] direction.

consists of a substitutional Pt atom and an interstitial Mn atom.

Figure 4 shows the ESR signals of Pt-Mn complex in the samples after thermal treatment at 400°C for 10 min, and at 400°C for 20 min in addition to the signals in as-diffused sample. The signal intensity is decreased by the dissociation of Pt-Mn complex due to the thermal treatment. The ESR signals of Pt-Mn complex are annihilated after thermal treatment at 400°C for 80 min. The behaviors of the ESR intensities of Pt-Mn complex for the isothermal annealing at 380°C, 400°C, and 450°C are shown in Fig. 5. The ESR intensities are normalized by  $I/I_0$ , where  $I_0$  corresponds to the ESR intensity of Pt-Mn complex in as-diffused samples. The ESR signals of Pt-Mn complex are annihilated at last by the thermal treatment. The ESR signals of isolated  $Mn^0_i$  can not be observed in the samples after the thermal treatment to dissociate the Pt-Mn complex. Moreover, an increase in the ESR intensity of isolated  $Pt^-_s$  due to the dissociation of Pt-Mn complex is not also observed. The isolated Pt and Mn atoms dissociated from the complex by thermal treatment can not be detected by the ESR measurements. The Pt-Mn complex is little formed from dissociated Pt and Mn atoms in range of temperature from 380°C to 450°C. The isothermal annealing behaviors of the ESR intensities are fitted by

$$I/I_0 = \exp(-t/\tau). \quad (1)$$

The fitting lines for the dependences of ESR intensities at 380°C, 400°C, and 450°C are represented in Fig. 5. The time constants are determined to be about 45 sec at 380°, 24 sec at 400°, and 8.3 sec for 450°, respectively. The arrhenius plot for the dissociation of Pt-Mn complex in Si is shown in Fig. 6. An activation energy for the dissociation of Pt-Mn complex is determined to be about 0.96 eV. The activation energy is near to the activation energy of about 0.70 eV for the diffusion of interstitial Mn in Si [15]. The diffusion of interstitial Mn atom in Si is much easier than that of substitutional Pt atom. It is expected that the Pt-Mn complex consisted of a

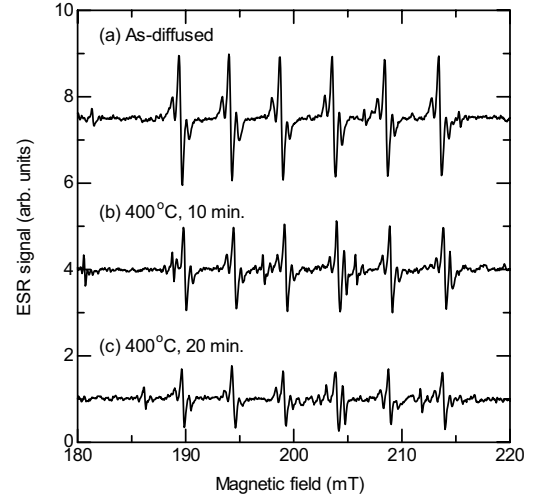


FIG. 4: The ESR signals of (a) as-diffused sample, and annealed samples at (b) 400°C for 10 min, and (c) 400°C for 20 min, respectively. The signal intensity is decreased by the dissociation of Pt-Mn complex due to the thermal treatment.

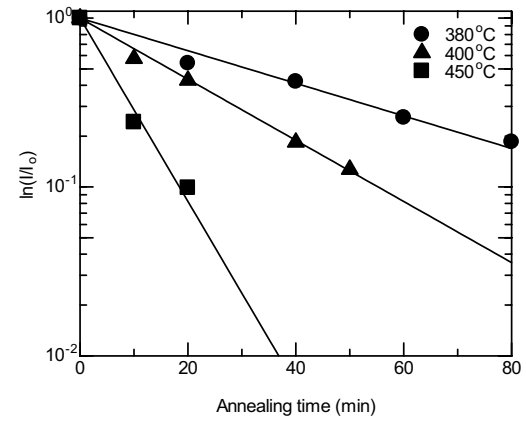


FIG. 5: The isothermal annealing behaviors of the ESR signal intensities of Pt-Mn complex. The normalized intensities for the annealing temperatures of 380°C, 400°C, and 450°C are indicated by filled circles, filled triangles, and filled squares, respectively. The lines fitted to exponential function are represented.

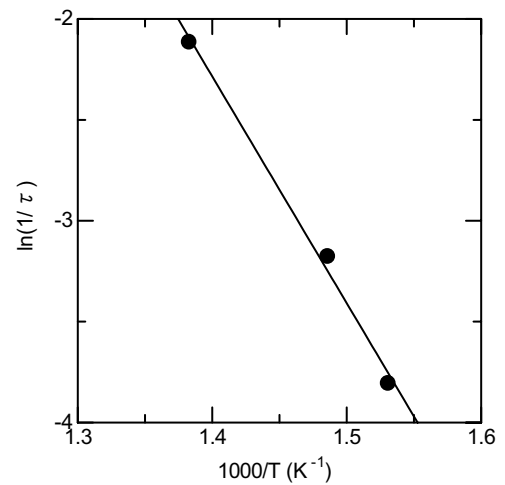


FIG. 6: Arrhenius plot for the dissociation of Pt-Mn complex in Si. The activation energy is determined to be 0.96 eV.

substitutional Pt atom and an interstitial Mn atom is principally dissociated by the removal of Mn atom from an interstitial site neighboring on a substitutional Pt atom. Moreover, the activation energy for the dissociation of Pt-Mn complex is a little higher than the activation energy for the diffusion of interstitial Mn. This is due to the binding energy between Pt and Mn atoms.

#### 4. Conclusion

We have investigated Pt-Mn complex in Si by the ESR measurement. The ESR signals of Pt-Mn complex are observed in both of n-type and p-type Si. The anisotropic g-values of  $g_{\parallel} = 2.2$ ,  $g_{\perp} = 2.1$  are obtained by analyzing the anisotropy of the ESR peak positions. The Pt-Mn complex is in the trigonal ( $C_{3v}$ ) symmetry with  $g_{\parallel}$  axis along  $\langle 111 \rangle$  direction. This indicates that the Pt-Mn complex consists of a substitutional Pt and an interstitial Mn atoms. Moreover, we have studied the dissociation of Pt-Mn complex by thermal treatment from 380°C to 450°C. The activation energy for the dissociation of Pt-Mn complex is determined to be about 0.96 eV from the arrhenius plot of the time constants of the decrease in ESR intensity due to the isothermal annealing. This value is a little higher than the activation energy for the diffusion of interstitial Mn atom in Si. This suggests that the Pt-Mn complex is dissociated by the removal of Mn atom from an interstitial site neighboring on a substitutional Pt atom.

#### REFERENCES

- [1] G. W. Ludwing and H. H. Woodbury, in Slid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1962), Vol.13, p. 223.
- [2] H. H. Woodbury and G. W. Ludwing, Phys. Rev. 126, 466 (1962).
- [3] P. Omling, P. Emanuelsson, and H. G. Grimmeiss, Phys. Rev. B36, 6202 (1987).
- [4] H. J. von Bardeleben, D. Stievenard, M. Brousseau, and J. Barrau, Phys. Rev. B38, 6308 (1988).
- [5] F. G. Anderson, R. F. Milligan, and G. D. Watkins, Phys. Rev. B45, 3729 (1992).
- [6] M. Höhne, Phys. Rev. B45, 5883 (1992).
- [7] P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, Phys. Rev. Lett. 70, 3816 (1993).
- [8] M. Höhne, U. Juda, Y. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, Phys. Rev. B49, 13423 (1994).
- [9] T. Mchedlidze, N. Fukata, and M. Suezawa, Jpn. J. Appl. Phys. 41, L609 (2002).
- [10] S. J. Uftring, M. Stavola, P. M. Williams, and G. D. Watkins, Phys. Rev. B51, 9612 (1995).
- [11] M. G. Weinstein, M. Stavola, K. L. Stavola, S. J. Uftring, J. Weber, J.-U. Sachse, and H. Lemke, Phys. Rev. B65, 035206 (2001).
- [12] Y. Kamiura, K. Sato, Y. Iwagami, Y. Yamashita, T. Ishiyama, and Y. Tokuda, Phys. Rev. B69, 0452061 (2004).
- [13] N. Fukata, T. Mchedlidze, M. Suezawa, and K. Saito, Phys. Rev. B66, 235209 (2002).
- [14] H. H. Woodbury and G. W. Ludwing, Phys. Rev. 117, 102 (1960).
- [15] W. Schröter and M. Seibt, in Properties of Crystalline Silicon, edited by Robert Hull (INSPEC, London, 1999), p. 543.