Relationship between Total Arsenic and Electrically Active Arsenic Concentrations in Silicon Produced by the Diffusion Process

Relationship between total arsenic and electrically active arsenic concentrations in silicon produced by the diffusion process

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The dependences of diffusion coefficient of As, D_{As}, upon total As concentration, C_T, and the relationships between C_T and resistivity ρ for several diffusion temperatures are experimentally obtained for the As diffusion into p-type Si from doped polycrystalline-Si sources in the temperature range 850–1050°C. It is found that the relationship between C_T and ρ is dependent upon diffusion temperature for C_T above 10^{20} cm^{-3}. The relationship between C_T and electrically active As concentration at diffusion temperature, C_A, i.e., $C_T = C_A + (3.2 \times 10^{-6}/n_i^3)C_A^4$ can be obtained, assuming that only electrically active As is mobile and is diffused by the single-level vacancy mechanism, and using the experimental result that the dependence of D_{As}/D_i (D_i is the intrinsic diffusion coefficient of As) upon C_T/n_i (n_i is the intrinsic electron concentration) is not influenced by diffusion temperature. Using the above equation, it is found that the relationship between C_A and ρ is independent of diffusion temperature, even for C_A above 10^{20} cm^{-3}, and can be approximated for C_A above 10^{20} cm^{-3} by an empirical equation: $\rho = 8.7 \times 10^4 C_A^{-2/5}$.

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I. INTRODUCTION

Accurate knowledge of high-concentration As diffusion in Si is important in the design of semiconductor device structures. A high-concentration As diffusion mechanism is, however, not clear since the accurate relationship between total As concentration, C_T, and electrically active As concentration, C_A, has not been obtained in spite of many works.[1-7]

Masters and Fairfield[1] have experimentally demonstrated that the diffusion coefficient of As, D_{As}, is linearly proportional to C_A below about 10^{20} cm^{-3} and have explained their experimental results by diffusion via a single-level vacancy mechanism.[8]

Kennedy and Murley[2] have reported that D_{As} reaches its maximum value at $C_T/n_i = 34$ (n_i is the intrinsic electron concentration at diffusion temperature) and decreases beyond it throughout the temperature range 950–1150 °C for the surface concentration ranging between about 8×10^{20} and 10×10^{20} cm^{-3}.

In order to explain the results obtained by Kennedy and Murley, in which D_{As} decreases with increasing C_T above $C_T/n_i = 34$, Chiu and Ghosh[3] have proposed to combine the double-level vacancy model and Hu's cluster model[4] in which the As cluster composed of four As atoms is formed in Si. In their model, D_{As} is not proportional to C_T below about 10^{20} cm^{-3}, which is not in agreement with the results of Kennedy and Murley.

Fair and Weber[5] have calculated D_{As} by combining the experimentally obtained relationship between C_T and C_A and the single-level vacancy model and have proposed the As-vacancy complex model in which the complex composed of two As atoms and a vacancy is formed in Si. Their relationship obtained experimentally between C_T and C_A is dependent upon the total As surface concentration, C_{T0}. The D_{As} obtained by their model is, therefore, dependent upon C_{T0}. Their model is effective for diffusions into n-type Si, but not into p-type Si. Based upon the model, Fair[6] has proposed that vacancy undersaturation due to the formation of As-vacancy complexes causes the cooperative diffusion effects, i.e., the retardation of B diffusion for sequentially diffused As and B layers in Si. However, comparing the data of Ref. 7 obtained by ion-implanted As sources with the data of Ref. 5 obtained by doped oxide sources mainly, it seems that D_{As} versus C_T, C_T versus C_A, and resistivity ρ versus C_T are dependent upon diffusion sources although the data obtained by ion-implanted As sources are somewhat different between Refs. 5 and 7.

Murota, Arai, Kobayashi, and Kudo[9] have reported that the relationship between C_T and C_A, and the dependence of D_{As} upon C_T, are not influenced by C_{T0} for the As diffusion into p-type Si from doped polycrystalline-Si sources, and the experimentally obtained relationship between C_T and C_A depends strongly upon the data of ρ versus C_A, which are varied in many investigators[7,10,11] for C_A above 10^{20} cm^{-3}.
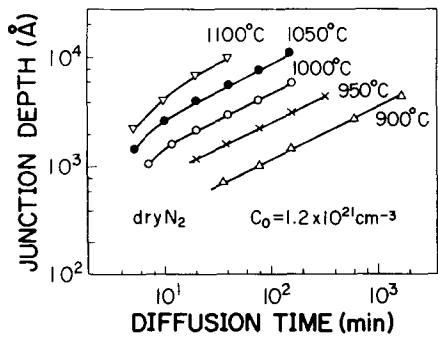
FIG. 1. Dependences of junction depth upon diffusion time for several diffusion temperatures.

To clarify the high-concentration As diffusion mechanism, it is necessary to obtain the accurate relationship between C_T and C_A. In the present work, the relationships between C_T and ρ and the dependences of D_{As} upon C_T for several diffusion temperatures are experimentally obtained for the As diffusion into p-type Si from doped polycrystalline-Si sources. Here, the doped polycrystalline-Si sources used have many advantages for the investigation of the As diffusion mechanism as follows: (i) The remarkable structural changes do not occur during the diffusion, differing from those of doped oxide sources,[12] (ii) the sources are the same phase as the substrate diffused, (iii) constant C_{T0} for diffusion time is kept, differing from the case of ion-implanted As sources. Moreover, assuming that only electrically active As is mobile and is diffused by the single-level vacancy mechanism, the relationship between C_T and C_A is calculated and the relationship between C_A and ρ is also obtained.

II. EXPERIMENTAL PROCEDURE

The As-doped polycrystalline Si as a diffusion source was deposited in an rf-heated reactor using the SiH_4-H_2-AsH_3 gas system. Deposition temperature on the wafer surface was 730 °C. The deposited thickness was about 4500 Å and the As concentration in polycrystalline Si, C_0, was $(1.05-1.20) \times 10^{21}$ cm^{-3}, which was determined by neutron-activation analysis described below. Substrates used were p-type Si wafers of 0.2–0.4 and 1–2 Ω cm with mirror polished (111) surfaces. Diffusion areas were defined by photolithography and chemical etching of polycrystalline Si. All diffusions were performed in the atmosphere of dry N_2 gas, where the surface of polycrystalline Si was covered with CVD SiO_2. The polycrystalline Si on the diffused layer was removed by the anodic oxidation method in H_3PO_4.

To obtain a profile of ρ in the diffused layer, measurements of sheet resistivity by a four-point probe method and removal of a thin layer of Si by the anodic oxidation method were repeated. Junction depths were obtained by the angle-lapping method, which was in good agreement with the anodic oxidation method. Profiles of total As concentration in diffused layers were obtained by neutron activation analysis. The samples, together with As_2O_3 as a comparative standard, were irradiated in the nuclear reactor JRR-4 in the Japan Atomic Energy Research Institute at a thermal neutron flux of 8×10^{13} n/cm^2 sec for 60 min. Radioactivity of

As in a thin layer of Si removed by the anodic oxidation method was measured by an 800-channel pulse-height analyzer with an NaI (Tl) detector.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS
A. Relationship between C_T and ρ, and the C_T dependence of D_{As}

The dependence of junction depth and sheet resistivity upon diffusion time for several diffusion temperatures are shown in Figs. 1 and 2. The junction depth and the reciprocal of sheet resistivity are proprotional to the square root of diffusion time and the product of junction depth and sheet resistivity is, therefore, constant for diffusion times above 10 min. This fact means that the electrically active As surface concentration, C_{A0}, in diffused layer is constant for the diffusion time because C_{A0} is determined only by the product of junction depth and sheet resistivity for As diffusion, as shown by Fair.[13,14] Based upon these results, D_{As} was determined by the Boltzmann-Matano method.[15]

Typical profiles of C_T and ρ in diffused layer for several diffusion temperatures are shown in Fig. 3. The relationships between C_T and ρ are obtained from the data presented in Fig. 3 and are shown in Fig. 4. The relationship between C_T and ρ is dependent upon diffusion temperature for the C_T above 10^{20} cm^{-3} and ρ increases with decreasing diffusion temperature. The dependences of D_{As} upon C_T, calculated from Fig. 3, are shown in Fig. 5. Maximum D_{As} and the C_T at maximum D_{As} decrease with decreasing diffusion temperature. The dependence of D_{As}/D_i (D_i is the intrinsic diffusion coefficient of As at the diffusion temperature) upon C_T/n_i for several diffusion temperatures, obtained from the data presented in Fig. 5, is shown in Fig. 6. D_i and n_i were calculated from Chiu and Ghosh's empirical formula[3] and Morin and Maita's empirical formula,[16] respectively, i.e.,

$$D_i = 24 \exp(-4.08 eV/kT), \tag{1}$$

$$n_i = 3.87 \times 10^{16} T^{3/2} \exp[(-1.21 + \Delta E_g)eV/2kT], \tag{2}$$

$$\Delta E_g = 7.1 \times 10^{-10} n_i^{1/2} T^{-1/2}.$$

From Fig. 6, it is seen that the dependence of D_{As}/D_i upon C_T/n_i is not influenced by diffusion temperature, and D_{As}/D_i increases proportionally with C_T/n_i to a maximum value of D_{As}/D_i and then decreases monotonically, and the maxi-
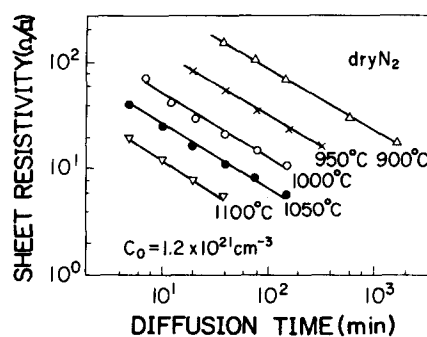

FIG. 2. Dependences of sheet resistivity upon diffusion time for several diffusion temperatures.
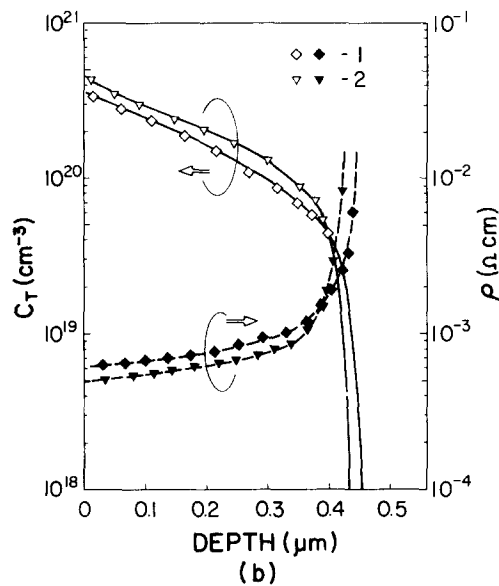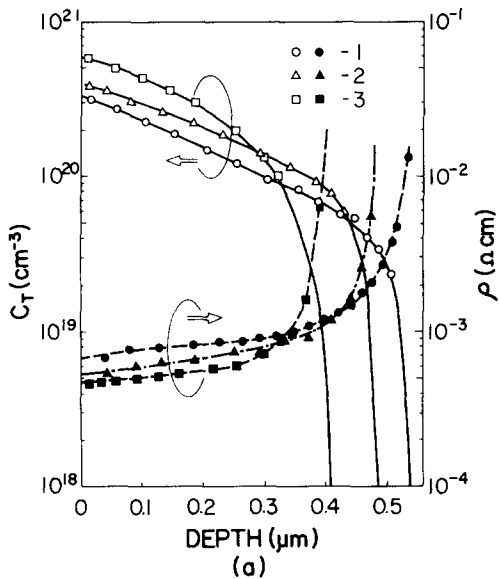
FIG. 3. Typical profiles of C_I and ρ in diffused layer for (a) curve 1—850 °C 12 575-min diffusion; curve 2—950 °C 425-min diffusion; curve 3—1050 °C 20-min diffusion (b) curve 1—900 °C 2020-min diffusion; curve 2—1000 °C 100-min diffusion.

mum D_{As}/D_i is 45 and the C_T/n_i at the maximum D_{As}/D_i is 35. These results agree well with the results of Kennedy and Murley, except that the D_{As}/D_i obtained in this work is somewhat larger than that of Kennedy and Murley for C_T/n_i above 35.

B. Relationships between C_T and C_A and between C_A and ρ

Under the assumptions that only electrically active As is mobile and is diffused by the single-level vacancy mechanism, D_{As} is given by

$$D_{As} = \frac{2D_i(C_A/n_i)}{\partial C_T/\partial C_A},$$ (3)

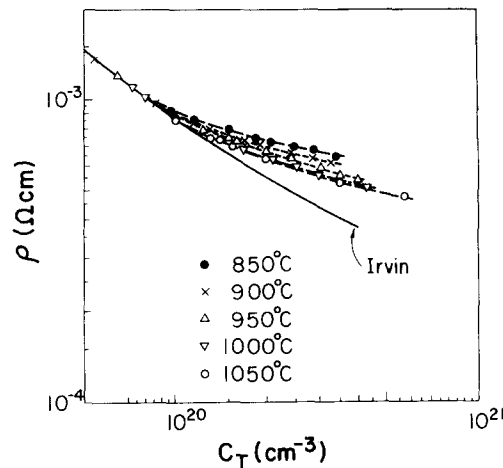where internal field effect and the Fermi-level effect in the

FIG. 4. Relationships between C_I and ρ in a diffused layer for several diffusion temperatures.

high-concentration region are also assumed.[4,5] Further, it should be noted that C_A in Eq. (3) is the electrically active As concentration at the diffusion temperature. Integrating Eq. (3), C_A becomes

$$C_A = n_i \left[\int_0^{C_I/n_i} \left(\frac{D_{As}}{D_i} \right) d \left(\frac{C_T}{n_i} \right) \right]^{1/2},$$ (4)

where $C_A = n_i$ is assumed for $C_T = n_i$. The relationship between $(C_T - C_A)/n_i$ and C_A/n_i, calculated from the data (solid line curve) presented in Fig. 6 and Eq. (4), is shown in Fig. 7. From Fig. 7, the relationship between C_T and C_A can be approximated by the empirical equation

$$C_T = C_A + (3.2 \times 10^{-6}/n_i^3)C_A^4.$$ (5)

Equation (5) is determined accurately only for C_T/n_i above 30 because it strongly depends upon the scatter of the data for C_T/n_i below 30. Equation (5) was derived from D_{As}/D_i versus C_T/n_i obtained experimentally, assuming Eq. (3). A
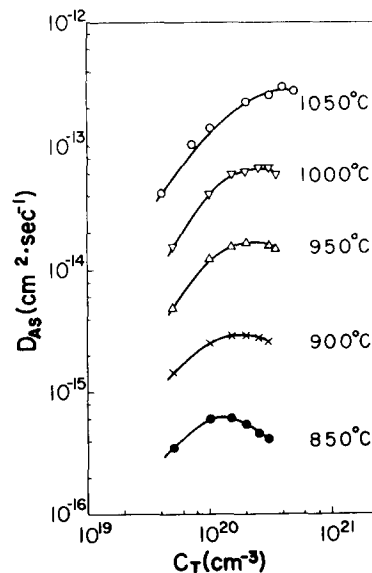

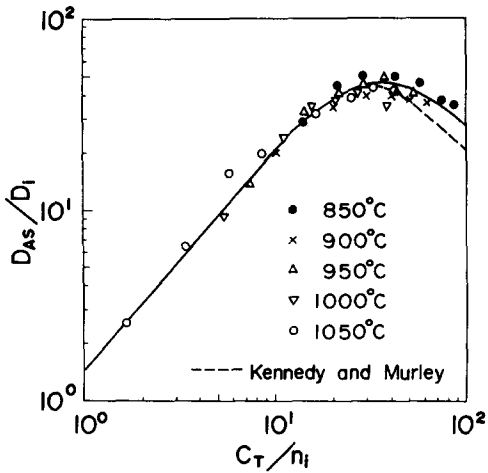FIG. 5. Dependences of D_{As} upon C_I for several diffusion temperatures.

FIG. 6. Dependences of D_{As}/D_i upon C_T/n_i for several diffusion temperatures.

FIG. 7. Relationship between $(C_T - C_A)/n_i$ and C_A/n_i, calculated from data presented in Fig. 6 and Eq. (4).

similar equation relating C_T to C_A was also derived from Fig. 4, assuming that C_A is equal to electron concentration at room temperature, n, and using the data of ρ versus n reported by many investigators.[7,10,11] As a result, it is obtained that the electrically inactive As concentration is proportional to C_A^4, which is the same as Eq. (5), but the coefficient of C_A^4 is larger than that in Eq. (5) and depends strongly upon the data of ρ versus n employed. Of all the ρ-vs-n data reported by many investigators, the data reported by Fair et al.[7] and Müller et al.[11] give a best fit to Eq. (5) for C_A below 3×10^{20} cm^{-3}. Based upon the above discussions, it is confirmed that the present method of deriving the relationship between C_T and C_A is very effective.

The relationship between C_A at diffusion temperature and ρ at room temperature, calculated from the data presented in Fig. 4 and Eq. (5), is shown in Fig. 8. Included in Fig. 8 is only the data of Irvin,[10] and not the data of Fair et al.[7] and Müller et al.[11] to avoid the confusions in the figure. The relationship between C_A and ρ is independent of the diffusion temperature, and ρ is determined only by C_A. It is, therefore, confirmed that the mobility of the free electron is independent of the electrically inactive As concentration. From Fig. 8, the relationship between C_A and ρ for C_A above 10^{20} cm^{-3} is approximated by

$$\rho = 8.7 \times 10^4 C_A^{-2/5}. \qquad (6)$$

Looking at Fig. 8 in more detail, ρ is proportional to $C_A^{-1/3}$ for C_A above 2×10^{20} cm^{-3} and is also approximated by the linear combination of $C_A^{-1/3}$ and C_A^{-1} above 10^{20} cm^{-3}; the physical meaning is not clear at present.

C. Behavior of vacancy and electrically inactive As

From the experimental results obtained by this work and Ref. 8, it is evident that (i) C_{A0} is constant for the diffusion time, (ii) the dependence of D_{As} upon C_T is not influenced by C_{A0}, and (iii) the electrically inactive As concentration, i.e., $C_T - C_A$, is independent of C_{A0} for any C_A specified and increases with increasing C_A [see Eq. (5)]. Based upon
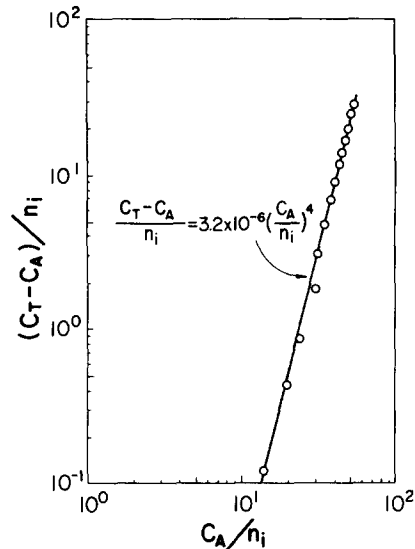
these As diffusion characteristics, the behavior of vacancy and electrically inactive As in the diffused layer is discussed.

The distribution of the vacancy concentration can be calculated numerically by solving the diffusion equation. First, it is assumed, as reported by Fair et al.,[5,6] that the electrically inactive As-vacancy complex is formed in the diffused layer and only the neutral vacancy is mobile and C_{A0} is constant for the diffusion time. The last assumption is different from the result reported by Ref. 6 and the same as that by Ref. 7. Then, the following diffusion equation in diffused layer is obtained:

$$D_{V^0} \frac{\partial^2 C_{V^0}}{\partial X^2} = \frac{\partial C_{V^0}}{\partial t} + \frac{1}{2} \frac{\partial (C_T - C_A)}{\partial t}, \qquad (7)$$

where D_{V^0} is the diffusion coefficient of the neutral vacancy and C_{V^0} is the concentration of the neutral vacancy. The solution of Eq. (7) shows that the vacancy undersaturation, that is, decrease of C_{V^0} with depth, occurs in diffused layer
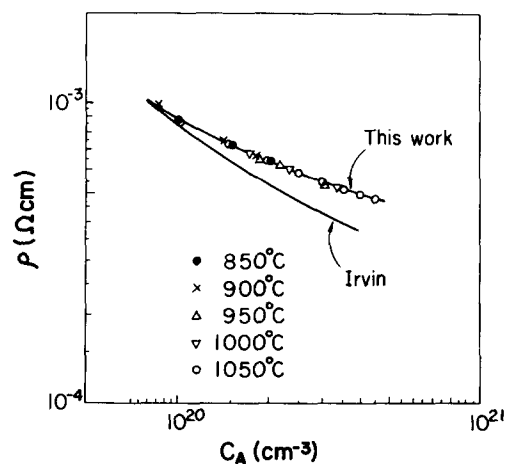

FIG. 8. Relationship between C_A at diffusion temperature and ρ at room temperature, calculated from data presented in Fig. 4 and Eq. (5).

due to the formation of the As-vacancy complex. The degree of the vacancy undersaturation increases with increasing C_{A0} because $C_T - C_A$ is determined by only C_A but not C_{A0} as described above, and C_A for a specified depth and diffusion time increases with increasing C_{A0}; as a result, the rate of As-vacancy complex formation, i.e., the second term on the right-hand side of Eq. (7) increases with increasing C_{A0}. These results mean that D_{As} is dependent upon C_{A0} and decreases with increasing C_{A0} for any C_T specified because D_{As} is determined by vacancy concentration. Therefore, the experimental results, that the dependence of D_{As} upon C_T is not influenced by C_{A0}, cannot be explained using the above assumptions. This result is not changed even if negatively ionized vacancy concentration calculated from C_{V^0} is taken into account. Consequently, the As-vacancy complex model, proposed by Fair et al., cannot be verified at present. Next, excess vacancy generation by E-center (As-vacancy pair) dissociation, proposed on the basis of the pair diffusion model,[17–19] is considered. For phosphorus diffusion, Yoshida et al.[18,19] have explained the phosphorus surface concentration dependence of the phosphorus diffusion coefficient assuming the excess vacancy generation by E-center dissociation. If this model can be applied for As diffusion, the amount of E-center dissociated must be small to depress the generation of excess vacancy. The association-dissociation mechanism of neutral and negatively ionized E-centers is, however, not clear at present. Therefore, the experimental result, that the dependence of D_{As} upon C_T is not influenced by C_{A0}, cannot be explained at present.

For the analysis of vacancy and electrically inactive As behavior in the As diffused layer, further investigation should be done.

IV. CONCLUSIONS

Conclusions obtained experimentally for the As diffusion into p-type Si from doped polycrystalline-Si sources are summarized as follows:

The relationship between C_T and C_A can be approximated by the equation $C_T = C_A + (3.2 \times 10^{-6}/n_i^3) C_A^4$, assuming that only electrically active As is mobile and is diffused by the single-level vacancy mechanism, and using the experimental result that the dependence of D_{As}/D_i upon C_T/n_i is not influenced by diffusion temperature. The above equation agrees with the one determined directly from the C_T-vs-ρ data, except for the coefficient of C_A^4.

The relationship between C_A and ρ is independent of diffusion temperature, although the relationship between C_T and ρ is dependent upon diffusion temperature, and can be approximated for C_A above 10^{20} cm^{-3} by the empirical equation: $\rho = 8.7 \times 10^4 \, C_A^{-2/5}$.

ACKNOWLEDGMENTS

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