Diffusion of vanadium in silicon

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(Received 15 October 1990; accepted for publication 15 January 1991)

The diffusion profiles of vanadium in silicon have been investigated. In the temperature range 950–1200 °C an in-depth profile measurement by deep level transient spectroscopy was used, and in the temperature range 600–800 °C an annealing experiment which employed a technique for profiling the concentration of deep levels within a depletion region was used. From the two kinds of concentration-profile measurements, the diffusion coefficient of interstitial vanadium in silicon was determined, and it is represented by the expression $D_V = 9.0\times10^{-3}\exp(-1.55/kT)\ \mathrm{cm^2\,s^{-1}}$.

Properties of $3d$ transition-metal impurities in silicon have received growing interest in recent years. Since most are fast diffusers, they influence the performance of silicon devices if introduced unintentionally during production. Therefore, gettering to eliminate these impurities from the active region of the device has been studied intensively.[1] In order to understand the gettering mechanism of transition metals, it is very important to know accurate diffusion data such as the solubilities and the diffusion coefficients. Hence, diffusion data from titanium to copper have been reported by many researchers, as summarized in Weber's review paper.[2] However, diffusion data for vanadium are very poor. In this letter, we report on the results of in-depth profile measurements by deep level transient spectroscopy (DLTS) for n-type silicon samples diffused with vanadium at temperatures between 950 and 1200 °C, and on the results of spatial distribution measurements using a profiling technique[3] based on DLTS for samples annealed in the temperature range of 600–800 °C. From these profile measurements, we show the temperature dependence of the solubility and the diffusion coefficient of interstitial vanadium in silicon.

The silicon substrates used were n-type float-zoned (111) silicon wafers with a phosphorus concentration of $2.2\times10^{13}\ \mathrm{cm^{-3}}$ for diffusion at 950, 1000, 1050, and 1100 °C, and of $1.0\times10^{14}\ \mathrm{cm^{-3}}$ for diffusion at 1150 and 1200 °C. The thickness of each wafer was about 0.12 cm. Vanadium was evaporated in a vacuum on both surfaces of the wafer by direct heating of a vanadium wire (99.95% purity) in which a large electric current was flowing. Each wafer deposited with vanadium was set in an evacuated quartz tube and heat-treated at a temperature between 950 and 1200 °C for a fixed period between 2 and 48 h in a vacuum and sequentially quenched to liquid-nitrogen temperature. The diffusion apparatus was similar to that described in Ref. 4. An in-depth profile measurement for the sample was performed by DLTS after etching the surface layer little by little and then forming the Schottky barrier with evaporated gold each time.

Three electron traps labeled NV1, NV2, and NV3 were recognized, as shown in Fig. 1. The energy level for trap NV1 was obtained as $E_c - 0.20$ eV by the rate-window variation method. Those for traps NV2 and NV3 were determined to be $E_c - 0.43$ eV and 0.49 eV by the nonlinear least-squares method,[5] which is useful for analysis of overlapping signals. Hall effect measurements showed that trap NV1 was an acceptor and traps NV2 and NV3 were donors. The energy levels of the acceptor-type trap NV1 and the donor-type trap NV2 are in good agreement with the values[2] for an acceptor level and a first donor level of interstitial vanadium. Thus, traps NV1 and NV2 can be assigned as an acceptor and a first donor of intersitial vanadium, respectively. As seen from an annealing experiment described later, trap NV3 completely disappeared in 20 μm surface region of the samples annealed in the range 600–800 °C though interstitial vanadium (traps NV1 and NV2) remained in that region. Thus, trap NV3 is due to a species other than interstitial vanadium. The problem for the assignment of NV3 requires further study.

We focused our attention on the concentration of trap NV1 (vanadium acceptor) and carried out in-depth profile measurements. The concentration was estimated from the peak height of the signal and the steady-state capacitance by using the method given in Ref. 6. The profiles of the concentration $N(x, t)$ at depth x are shown in Fig. 2, where l is the sample thickness and t the diffusion time. The profiles are well described by the solution[7] of Fick's equation assuming a constant surface concentration at $x = 0$ and $x = l$, which corresponds to the solubility N_V of interstitial vanadium. The fits of the experimental data to

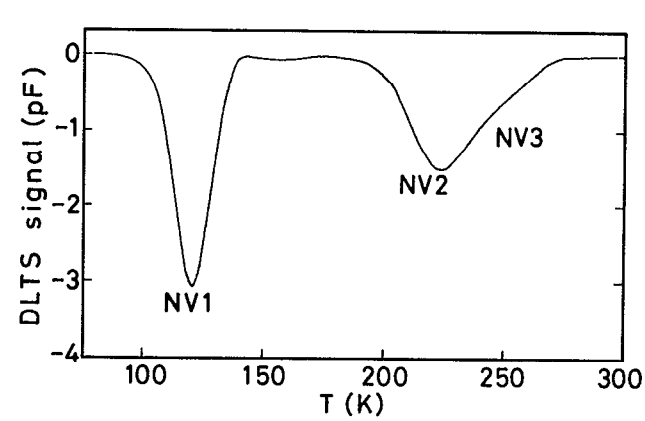

FIG. 1. DLTS spectrum for n-type silicon doped with vanadium at 1200 °C for 8 h. The reverse bias is 5 V, filling bias 0 V, rate window $t_1/t_2 = 0.5/5$ ms, and injection pulse width 200 μs.

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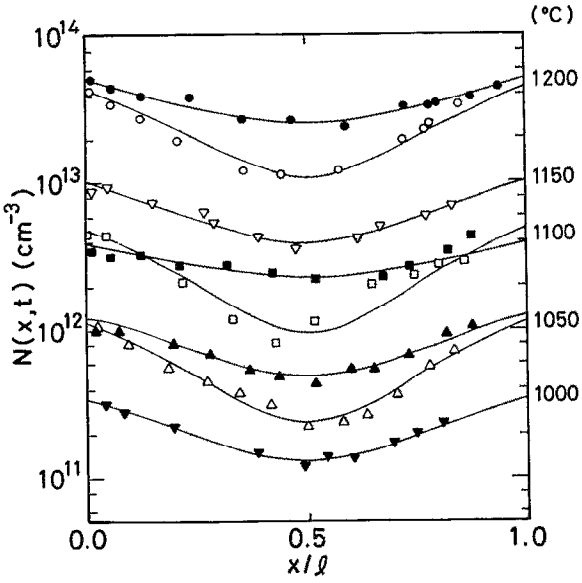

FIG. 2. In-depth profiles of the concentration of trap NV1. (○) 1200 °C, 4h ($l = 0.117$ cm), (●) 8 h (0.117 cm), (▽) 1150 °C, 12 h (0.121 cm), (□) 1100 °C, 8 h (0.109 cm), (■) 16 h (0.111 cm), (△) 1050 °C, 12 h (0.118 cm), (▲) 24 h (0.118 cm), (▼) 1000 °C, 38 h (0.111 cm).

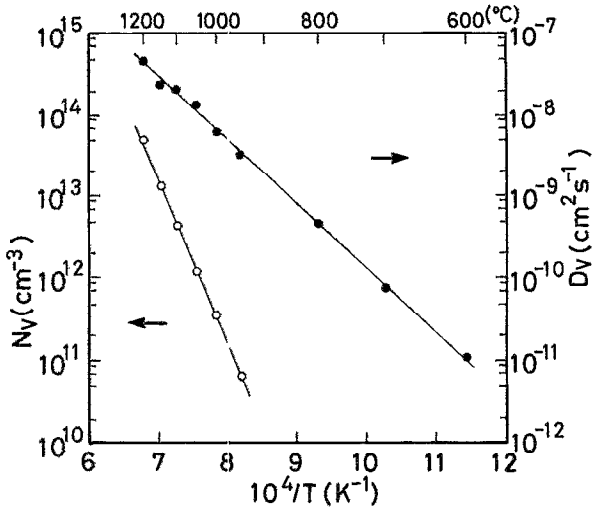

FIG. 3. Temperature dependence of the solubility N_V (○) and the diffusion coefficient D_V (●) of interstitial vanadium in silicon.

the solution are shown by solid lines in Fig. 2. The fit yields the solubility N_V and the diffusion coefficient D_V, and the obtained values are listed in Table I. The values of N_V are plotted in Fig. 3 as a function of diffusion temperature. It can be represented by the expression

$$N_V = 3.0 \times 10^{27} \exp(-4.04/kT)\ \text{cm}^{-3}, \qquad (1)$$

where k is the Boltzmann constant (eV/K) and T the absolute temperature (K). The solubility is considerably lower than those of other transition elements such as manganese and iron.[2]

We also performed an annealing experiment at lower temperatures to determine the diffusion coefficient D_V in a wide temperature range. The starting material was a wafer ($l = 0.06$ cm) diffused with vanadium at 1170 °C for 24 h, which insured a uniform distribution. After fabrication of an evaporated gold Schottky diode, the concentration profile of trap NV1 within the depletion region was measured with the profiling technique[3] of DLTS (bias condition: reverse bias 40 V, filling pulse heights ranging from 2 to 39 V in 1 V increments) The barrier metal (Au) was then removed with aqua regia, and the sample was annealed at each temperature of 600, 700, and 800 °C for a fixed period between 0.5 and 83 h; and the Schottky diode fabrication and the spatial distribution measurement were performed again. Figure 4 shows the results for the samples annealed at 700 °C. The sample without annealing has a uniform distribution, and the concentration 2.2×10^{13} cm^{-3} is in good agreement with Eq. (1) at 1170 °C. By contrast, the concentration profiles for annealed samples show gradual decrease with decreasing distance x, suggesting the out-diffusion of vanadium. Thus, it can be assumed that the diffusion equation for the annealing process, as well as in-diffusion, is given by Fick's equation with the initial condition $N(x,0) = 2.2 \times 10^{13}$ cm^{-3} and the boundary condition $N(0,t) = N_{an}$, where N_{an} is the solubility given by Eq. (1) at the annealing temperature. The solid lines in

TABLE I. Values of N_V and D_V for vanadium in silicon.

Temperature (°C)	Time (h)	$10^{-12} \times N_V$ (cm^{-3})	$10^{11} \times D_V$ (cm^2 s^{-1})
1200	2, 4, 8	49 ± 5	4700 ± 300
1150	6, 12	13 ± 3	2400 ± 100
1100	8, 16	4.4 ± 0.4	2100 ± 200
1050	12, 24	1.3 ± 0.1	1400 ± 200
1000	38	0.35	620
950	48	0.065	340
800	0.5	···	47
700	0.5, 2, 8	···	8.0 ± 0.9
600	21, 83	···	1.10 ± 0.02

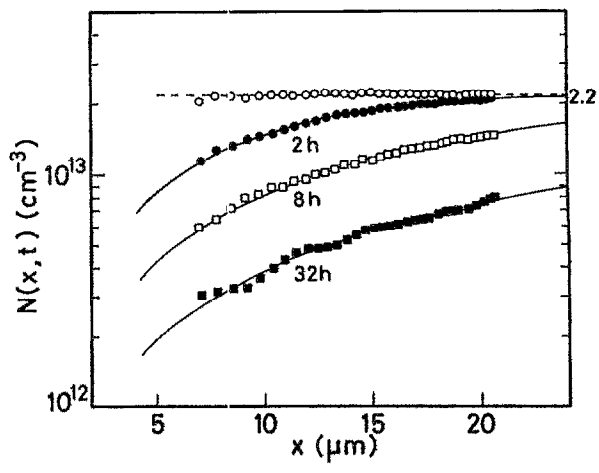

FIG. 4. Concentration profiles of trap NV1 in samples annealed at 700 °C for 0 h (○), 2h (●), 8 h (□), and 32 h (■). The starting material is a sample in-diffused with vanadium at 1170 °C for 24 h.

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Fig. 4 represent the profiles fitted to the solution of Fick's equation with just one parameter D_V. We could thus determine the value of D_V for the sample annealed at 700 °C. The values obtained at 600 and 800 °C, as well as at 700 °C, are listed in Table I. The diffusion coefficients, D_V, deduced from two kinds of concentration-profile measurements are plotted in Fig. 3 as a function of diffusion temperature. It can be represented by

$$D_V = 9.0 \times 10^{-3} \exp(-1.55/kT) \mathrm{cm}^2 \mathrm{s}^{-1}. \quad (2)$$

The activation energy of 1.55 eV is very consistent with the trend of migration enthalpies[8] of other 3*d* transition-metal impurities.

In summary, diffusion data of interstitial vanadium in silicon have been obtained from two kinds of concentration-profile measurements. The diffusion coefficient has been determined in a wide temperature range of 600–1200 °C, and it is very consistent with the trend of those for other 3*d* transition-metal impurities.

The authors would like to thank Professor Kimio Hashimoto of Kurume Institute of Technology for his encouragement and valuable discussion in this work.

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