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DIFFUSION OF TELLURIUM IN SILICON

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Abstract

Diffusion of Te in Si was studied by a radiotracer technique using ^{121}Te produced and on-line implanted at the ISOLDE facility at CERN and by spreading-resistance measurements after diffusion from the vapour phase. Penetration profiles of Gaussian type and of erfc-shape were found, respectively, corresponding to the actual boundary conditions. Diffusion coefficients from both experiments show an excellent agreement. Remarkable is the pronounced curvature observed in the Arrhenius diagram. Another striking feature of the present work is the occurrence of diffusion profiles with an exponential dependence on the penetration depth.

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INTRODUCTION

For several reasons the chalcogens have been examined as dopants in Si rather extensively by infrared absorption, DLTS, EPR/ENDOR and Hall-effect measurements (see [1] for an overview). By contrast, the number of accurate diffusion studies on S, Se or Te is limited. Nevertheless, the data in the literature reveal an interesting feature, i.e., the penetration rates of three chalcogens (O, S and Se) are situated within the wide gap between the small substitutional diffusivities of the shallow dopants, like B or P, and the large diffusion coefficients of interstitially dissolved foreign atoms, like Fe or Li, while the slowest migrating group-VI element, Te, represents a borderline case [2]. This may indicate that the diffusion of chalcogens in Si involves exchanges between interstitial and substitutional sites like observed for Au or Pt [3-5]. Therefore diffusion studies may also contribute to solve the question how chalcogens are incorporated in the Si matrix.

The present work is part of a research program concerning the diffusion properties of S, Se and Te in Si. First data on Te are presented, which include the results of two different experimental techniques.

EXPERIMENTAL

RADIOTRACER TECHNIQUE

Depth distributions of the total Te content were measured with the aid of ^{121}Te . This radioactive isotope with a half-life time of 16.8 d was obtained after implantation (60 keV, dose $\leq 10^{17} \text{ m}^{-2}$) of its rapidly decaying grandmother nuclide ^{121}Xe at the ISOLDE facility at CERN [6]. ^{121}Xe was produced by irradiating a lanthanum carbide target with 600 MeV protons from the CERN synchro-cyclotron. The main advantage of this method is the availability of the tracer in a very pure form with the highest possible specific activity, so that extremely low Te concentrations can be detected. Diffusion anneals were performed in sealed quartz ampoules under argon atmosphere. Penetration profiles were determined by means of serial sectioning using a precision lapping device for deep penetrations ($>30 \mu\text{m}$) and ion-beam-sputtering for shallow ones ($<1 \mu\text{m}$). Counting of the section radioactivity was performed by standard methods employing NaI- or Ge-detectors.

SPREADING-RESISTANCE TECHNIQUE

Penetration profiles of electrically active Te were determined with the aid of the spreading-resistance (R_s) technique [3,7]. In these experiments Si crystals were diffused from the vapour phase by introducing high-purity Te into the quartz ampoules. In order to reduce gas transport of sample material inside the ampoule small amounts of Te (0.3-2 mg) were weighed-in.

A typical R_s -profile is shown by figure 1. Penetration of Te is reflected by the lowering of the resistance near the surface, whereas the constant R_s level at depths greater than $35 \mu\text{m}$ corresponds to the resistivity of the as-grown Si material.

Conversion of R_s -profiles to concentration profiles was based on the two dominating energy levels of Te in Si, i.e., 0.199 eV and 0.411 eV below the conduction band edge [1]. Hereby double-donor statistics were applied [8] and allowance was made for the dependence of the electron mobility on the charged impurity concentration [9]. Following other authors [1,8] it is assumed that the above energy levels can be associated with isolated substitutional Te_s atoms.

Figure 1 - Spreading-resistance (R_s) profiles measured on $3 \Omega\text{cm}$, phosphorous-doped Si after Te diffusion at 1407 K. By conversion of the R_s -data the shallow C_s -profile of figure 3 is obtained.

RESULTS AND DISCUSSION

PENETRATION PROFILES OF GAUSSIAN SHAPE

Radiotracer measurements were carried out for diffusion temperatures between 1186 K and 1629 K. Typical profiles are shown in figure 2 as $\log C_{Te}$ vs. x^2 plots. These profiles are compared to the thin-film solution of Fick's second law for a constant diffusion coefficient (straight lines). The good fits are consistent with the circumstance that the implantation depth is negligible small (projected range: 30 nm) in comparison with the penetration distances. Figure 2 also reveals extremely small absolute concentrations with great-depth values as low as 10^{16} m^{-3} .

Figure 2 (left) - ^{121}Te profiles of gaussian type. (1365 K, 241 h, $C_s(0)=8.9 \times 10^{18} \text{ m}^{-3}$; 1429 K, 264 h, $1.5 \times 10^{20} \text{ m}^{-3}$; 1480 K, 120 h, $8.5 \times 10^{20} \text{ m}^{-3}$; 1561 K, 40.2 h, $7.9 \times 10^{19} \text{ m}^{-3}$)

Figure 3 (right) - Te_s profiles of erfc-type (1407 K, 238 h; 1505 K, 119 h; 1557 K, 119 h)

PENETRATION PROFILES OF ERFC-SHAPE

Spreading-resistance measurements were done after diffusion anneals in the temperature range 1407-1557 K. Te_s distributions shown in figure 3 as $\log C_s$ vs. x plots are well described by the erfc-function (solid lines), which represents the theoretical profile in the case of Te -saturated boundaries. Correspondingly, the C_s values at $x=0$ may be considered as Te_s solubilities characteristic for the vapour pressure during the diffusion anneal. The present $C_s(0)$ data are compatible with a saturation concentration at 1473 K determined from Hall-effect measurements [8]. However, our experiments reveal not-monotonic variations of the boundary concentration with annealing temperature as well as with the weighed-in amount of Te . This phenomenon is also apparent in the work of Janzén et al. [2].

DIFFUSION COEFFICIENTS

Figure 4 shows that the diffusivities extracted from the profiles of ^{121}Te (circles) and Te_3 (squares) agree very well, whereas they are larger than the SIMS data of Janzén et al. [2] (triangles). Although in the latter work the annealing conditions were similar as in our electrical experiments, deviations from the erfc are reported (see below). Therefore, one may doubt whether these D -values are comparable to the present data.

The solid line in figure 4 serves to guide the eye. Besides it represents a fit of the sum of two Arrhenius terms to the radiotracer data. The goodness of this fit might indicate that the Te diffusion occurs by two mechanisms, e.g., a vacancy mechanisms predominant at lower temperatures and an interstitial-cy mechanism being important in the high-temperature regime. This has been proposed for Si self-diffusion [10], while it appears to be accepted now that also the migration of the group-III and group-V elements proceeds by vacancies and self-interstitials [11]. Although the diffusivity of Te is similar to that of the group-III acceptors, the above picture has to be rejected, since the activation energies resulting from the two-exponential fit, 2.33 ± 0.08 eV and 5.92 ± 0.33 eV, and the pre-exponential factors associated with them, $1.9 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $2.1 \times 10^4 \text{ m}^2 \text{ s}^{-1}$, are too small and too large, respectively.

Remarkably the present 2.33 eV is of about the same magnitude as the activation energies reported for the other chalcogens [1] whose diffusion rates are too fast, however, to be compatible with a purely substitutional mechanism. Therefore it appears probable that the migration of Te, as well as Se or S, involves exchanges between an interstitial (Te_i) and a substitutional (Te_s) configuration. Since such exchanges are mediated by vacancies (dissociative mechanism [12]) or self-interstitials (kick-out mechanism [13]) the penetration rate of the most stable configuration, Te_s , is controlled by the transport properties of either these intrinsic point defects or Te_i [3]. In the former case the diffusivity of Te_s should be related to Si self-diffusion (as found for Au or Pt [3,4]), which can readily be shown not to be true for the present data. Therefore the latter case (Te_i -limited diffusion) may be realized implying that the effective Te_s diffusivity is written as

$$D_s^{\text{eff}} = C_i^{\text{eq}} D_i / (C_s^{\text{eq}} + C_i^{\text{eq}}). \quad (1)$$

The notion that the solubility (C_s^{eq}) of Te_s goes through a maximum whereas the diffusivity (D_i) and presumably also the extremely low solubility (C_i^{eq}) of Te_i will obey an Arrhenius law up to the melting point, may explain in this model the upward curvature at high temperatures in figure 4. Analogous explanations can be given for curvatures in the $\log D$ vs. $1/T$ plots of Ge:Cu and Si:Au for which the interstitial-substitutional diffusion has been well established [14].

Figure 4 - Arrhenius plot of the Te diffusivity in Si (○ ^{121}Te data, □ R_s -data, both from this work; ▽ SIMS data [2])

PENETRATION PROFILES OF EXPONENTIAL SHAPE

Figure 5 reveals a shallow ^{121}Te profile measured by sputter-sectioning at a low temperature. Surprisingly this profile is linear over two decades in a $\log C_{\text{Te}}$ vs. x representation. Similar profiles which even cover much wider concentration intervals were determined from electrical measurements (figure 6). Also the SIMS profile presented by Janzén et al [2] exhibits on closer inspection an exponential x -dependence, although these authors have fitted their data by the erfc in a manner as demonstrated by the dashed line in figure 5. The present results, however, appear to confirm that we are dealing here with a real phenomenon. This is further supported by our preliminary data on Si:S.

Figure 5 (left) - Redistribution of an implanted ^{121}Te profile after a 5.67 h anneal at 1056 K. Dashed line: erfc -dependence.

Figure 6 (right) - Diffusion profiles of Te_2 from R_{S} -measurements (1407 K, 238 h; 1482 K, 119 h). Dashed line: Te -pair model.

In searching for the reasons for the exponential profiles one might think of the possibility that (i) the matrix evaporates at a high rate [15]. Although at the highest temperatures loss of Si was observed on samples diffused from the vapour phase, profiles were measured on those parts where the original thickness was retained. Moreover, evaporation effects were not seen on implanted crystals. Also pipe diffusion via (ii) dislocations [16] or (iii) grain boundaries ($\log C \sim x^{6/5}$) [17] can be excluded, since our samples consisted of dislocation-free, monocrystalline Si. Furthermore, generation of dislocations during diffusion has not occurred as checked by preferential etching. A possible explanation given in the literature for Ge:Ag [18] involves (iv) the presence of deep traps from which the diffusant cannot escape. Apart from the difficulty to identify the nature of these traps in our specimens most of which contained extremely low carbon ($\leq 5 \times 10^{20} \text{ m}^{-3}$) and oxygen ($\leq 3 \times 10^{21} \text{ m}^{-3}$) concentrations, the exponent in this model does not depend on annealing time. This contradicts our findings on Si:S where owing to a much faster diffusivity the time dependence was readily established. Moreover, it would be hard to understand why exponential- and erfc -type penetrations are very similar (cf. the 1407 K-profiles in figures 3 and 6). Recently chalcogen pairs are the subject of intensive research [1,19]. This makes it tempting to seek a solution by assuming that (v) pair formation takes place during diffusion, e.g.

(V-vacancy, I-self-interstitial, Te_{2s} -pair of neighbouring Te_s atoms). Indeed, the profile predicted by this model (dashed line in figure 6) on the basis of $D_{2s}^{\text{eff}} - (C_{2s}/C_s^{\text{eq}})^{-1/2}$ closely follows an exponential dependence over two orders of magnitude. However, the deviations at great depths cannot be overlooked. Assuming that D^{eff} is only dependent on concentration (vi) a formal solution is found as

$$D^{\text{eff}} = D^* (1 - \ln C/C_0) \quad (3)$$

where D^* is a constant and $C_0 = C(x=0)$. Although equation 3 would produce profiles of the form $C = C_0 \exp[-x/(2D^*t)^{1/2}]$, it is not clear from what mechanism this D^{eff} could arise.

A key to the interpretation of the exponential profiles may come from the observation that the boundary concentrations of these profiles are high. This is not only true for the radiotracer measurement in figure 5 where probably all C_{Te} values lie above the solubility limit at 1056 K, but also for the exponential C_s -profiles as is seen from a comparison of the 1407 K-plots. In conclusion, no satisfactory explanation for occurrence of the exponential-type Te profiles can be presented at the moment. More research needs to be done, including the combined application of different experimental techniques.

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