INVESTIGATION OF THE DIFFUSION INTO Si OF Au VIA FRANK-TURNBULL MECHANISM BY MONTE CARLO SIMULATION*

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ABSTRACT

VIDSIM[1] (Vacancy and Interstitial Diffusion Simulator), a program for Monte Carlo simulation of point defect diffusion and interaction in diamond and zinc-blend crystal structures has been developed and used to carry out some fundamental studies in Si and AlGaAs. We report here the latest result of a computer simulation designed to examine the diffusion into Si, in the presence of vacancy (V) clusters, of Au or similar transition metals that migrate mainly as interstitials but reside as substitutional impurities. Frank-Turnbull mechanism is assumed in the diffusion process. Also, we investigate the effect of vacancy (V) clusters distributed in the sample on the profile. Au distribution of both interstitials (Au_i) and substitutionals (Au_{Si}) are presented.

I. INTRODUCTION

People have been showing great interest in doing research on diffusion in semiconductors because of its importance in industry as well as in science. A variety of models for point defect migration, interaction and reaction have been proposed and a great amount of theoretical work has been done to account for, in one way or another, experimental results or observations. Yet, there is much controversy over the validity of the models or mechanisms, such as kick-out (KO)[2] and Frank-Turnbull (FT)[3] mechanism, because we believe, there have been no rigorous connections between atom level assumptions and macroscopic consequences prior to our simulation program. For most differential equations which describe the diffusion processes, there exist no analytical solutions.

VIDSIM has been developed to resolve the relation between atom level assumptions and macroscopic consequences. It assumes no differential equation. It uses an atom level Monte Carlo algorithm and involves an enormous amount of computation to obtain statistically significant results. The program models the evolution of a user-defined initial set of defects in space and time for any mechanisms the user chooses to simulate. The complex relationship between assumptions and consequences is thus obtained without any of the approximating passage to limits that have confused the previous literature. We have previously published direct simulations of the KO mechanism, for the set of assumptions advocated by those who suggest it accounts for Au diffusion into Si, which showed that the true result is very different from that expected by those advocates[4,5].

We notice[5,6] that much needs to be understood in the diffusion process involving vacancies as well as clusters of them. We report here our latest work on a computer simulation designed to examine the diffusion into Si of Au via Frank-Turnbull mechanism in the presence of vacancy clusters. Results are applicable to Cu or Pt or similar transition metals, which, like Au, migrate mainly as interstitials but reside primarily as substitutional impurities.

II. SIMULATION SET-UP

This particular simulation assumes that no Si self interstitials, Si_i's are initially present and none can be produced during the diffusion process, that there are vacancies initially present as clusters in the bulk and that single vacancies can be created and annihilated at the surfaces normal to the x direction. It also assumes that a source of Au_i is on the normal surface of the positive x boundary where Au_i will be annihilated if it returns there, and a reflexive boundary condition for Au_i is imposed on the far side, i.e., the negative x boundary. While vacancies are generated at a rate of 1.84×10^{-9} per surface site per attempt period (a.p.), which, in Si, is estimated to be 74 fs, the zone boundary phonon period, the Au_i source injects Au_i on the surface at a rate of 1.84×10^{-9} per attempt period per surface site or 184 injections (on average) per diffusion step $r \equiv 5 \times 10^6$ a.p.. The sample simulated is 2000 a thick in x direction and 100 a both in the y and z directions, where a is the lattice constant for the material of interest. Periodic boundary conditions are imposed on the y and z directions. Initially the sample is perfect except for 19 clusters of 5 V's (V_5) each spaced at 100 a intervals in the x direction through the bulk of the sample, which corresponds to a concentration $[V] = 3.0 \times 10^{16}$ cm^{-3}, a conservative estimated of $[V]$ at the melting temperature based on the positron lifetime results reported by Dannefaer et al[7].

We assert that the above conditions are appropriate for the case that Au-Si molten alloy has formed on one side and that an amorphous thermal oxide layer, with no molten alloy, is present on the far side.

We collect an ensemble of 20 of the sample runs of simulation, each of which extends to 240 steps of 5×10^6 a.p. i.e., 12×10^9 a.p.. There were a total of about 6.25×10^{10} atomic hops in the simulation. Of the 8.75×10^5 Au atoms injected, 1289 are retained as Au_{Si} and 224 are retained as Au_i at the end. Of 1.75×10^6 vacancies injected, 3075 are retained. Note that less than 0.2% of the defects that are introduced survive at the end of this simulation.

III. RESULTS OF COMPUTER SIMULATION AND DISCUSSIONS

We show in Table 1 the rates at which vacancy clusters of various sizes emit V's and diffuse for a particular set of atom level assumptions[1].

We observe that, for the simulation of clusters of type V_5, most of the original clusters break up into single vacancies after 4 r simulation time; they do not migrate a significant fraction of the 100 a initial minimum spacing between them before they totally disperse. Those scattered V's from the original clusters join newly diffusing-in V's from the surfaces and can form new clusters of various sizes. Simulation shows that there are clusters of size of 6, 7, 8 and 9 that form spontaneously from single vacancies during the process. We notice that there are "magic numbers" for which small clusters are particularly stable, e.g., n = 6. Some of these also diffuse very slowly. We suppose that small clusters of such size account for the 450 ps signal observed in many, but not all positron annihilation spectra[8]. We also study the sample with a 17 V (V_{17}) cluster initially present and find that the simulation requires a great deal of commuter effort because there is so much atomic diffusion around the surface of the cavity. Having simulated a total time of 20 r, we have observed no emission of any V from such a cluster. Thus, we conclude that the mean time to emit a V exceeds 5 r. These clusters also diffuse very slowly. We suggest that such large

Table 1. Diffusivity and mean time to emit one or more vacancy from clusters of n vacancies. Time unit $r \equiv 5 \times 10^6$ a.p.. These values result from the parameters assumed[1].

n=	1	2	3	4	5	6	7	8	17
$D_n(a^2/r)$	1177	594	559	419	236	4.0	47	171	1.5
E_n (r)	--	0.66	0.39	0.41	0.35	11.3	3.25	2.25	> 5

clusters correspond to the 1.5 ns signal in all positron annihilation spectra and for the D defects that are so difficult to anneal out[9].

We observe that more vacancy clusters of various sizes larger than divacancies are found to be on the far side of the sample, which might result from the asymmetric Au injection that gives rise to more break-up of clusters by Au_i near the source side. For example, referring the vacancy distribution at step 160, as shown in Fig.1, we see a peak at the location somewhere around 1650 a, i.e., about 350 a from the far surface. Investigation shows that the vacancy clusters, esp. of size 6, (V_6) which is surprisingly stable, are responsible for the sharp rise in the profile. Distribution of V_6 at several steps are shown in Fig. 2.
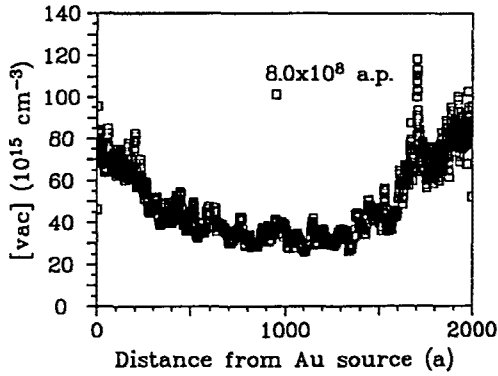

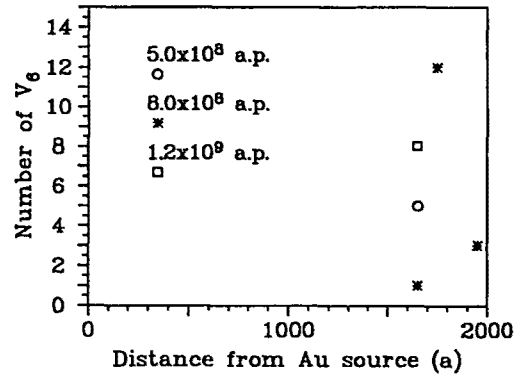Fig. 1. The profile of vacancy concentration in the sample at step 160.

Fig. 2. Vacancy clusters of type V_6 observed at step 100, 160 and 240.

In Fig. 3 we show the profile of divacancies, [V_2], which demonstrates a U shape. Since the [V](x) for single vacancies is not uniform, as shown in Fig. 1, some variation in [V_2] as predicted from the Law of Mass Action if "local equilibrium" is assumed. This would imply [V_2] should vary as $([V])^2$. Also, it is obvious that [V_2] profile should dip at the sample surfaces because annihilating boundary conditions for vacancies are imposed. Fig. 4 shows a profile of Au_{Si} for t = 1×10^8, 2×10^8, 4×10^8, and 1.2×10^9 a.p., and Fig. 5 demonstrates the distribution of Au_i concentration through the sample at the same time period as in Fig. 4.
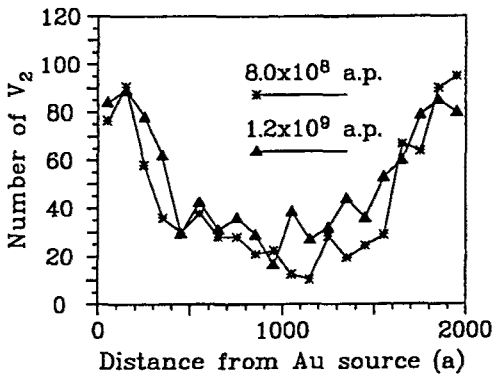

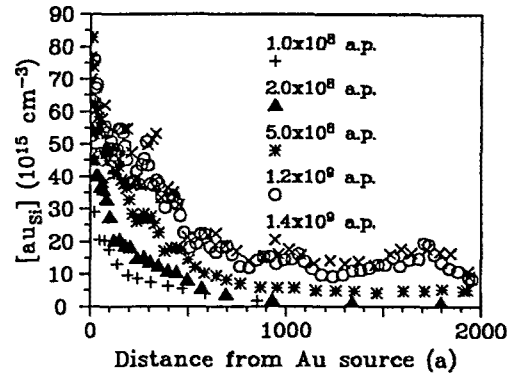Fig. 3. The profile of divacancies, V_2 in the sample, observed at step 100 and 240.

Fig. 4. The profile of Au substitutionals in the sample, observed at step 20, 40, 80 and 240.

From the Fig. 4 and Fig. 5, we see the distribution of Au_i is similar to that of Au_{Si} and not much more uniform despite the fact that the Au_i have a diffusivity of 22,894 a^2 r^{-1}, 19 times the diffusivity of the V's and dramatically larger than the effective diffusivity of Au_{Si}'s. The ratios of concentrations on both surfaces for both Au_{Si} and Au_i are observed to be about the same, which is similar to the result we reported when we simulated Au diffusion into Si assuming KO model[3,4]. In simulating KO model, we allowed no V's and made the Si_i's diffuse less rapidly than the Au_i's. However, there is no rise of [Au_{Si}]

near the far surface. The results shown in Fig. 4 are contrary to the assertions or assumptions of many previous investigators, particularly those who advocate the KO mechanism. In contrast to the monotonic distribution of Au_i shown in Fig. 4, they assert that since the Au_i diffuses so rapidly, a uniform distribution of Au_i will be established from the very beginning of the diffusion. We also note that the $[Au_i]$ rises with $[Au_{si}]$ at the far side and the profile of $[Au_i]$ tends to be flat at the far side as simulation time elapses. The flatness of $[Au_i](x)$ near the far end is a result consistent with the reflexive boundary conditions used in our simulation.

In Fig. 6 we show the variation of $[Au_{si}]$ in the center versus the square root of time. The trend shown is not exactly that as reported in previous literature. Two distinctions are found. First, the best fit of linear regression shows that the best straight line does not pass through the origin, as the previous authors'
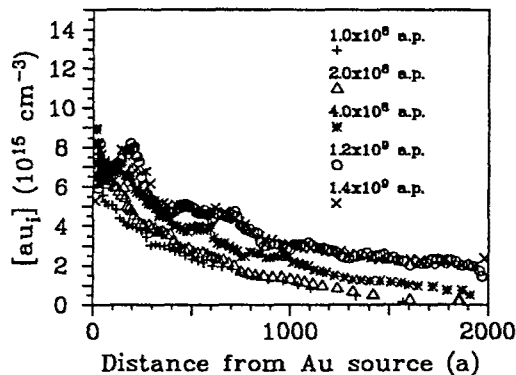

Fig. 5. The profile of Au interstitials in the sample, observed at step 20, 40, 80 and 240.
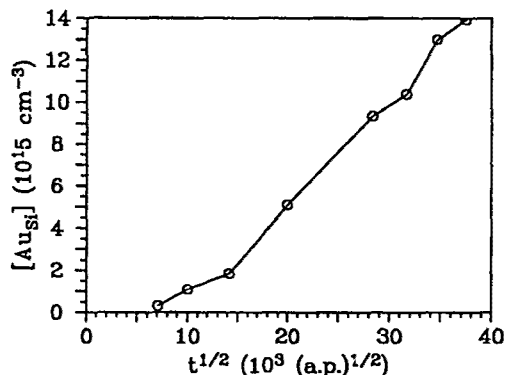

Fig. 6. The variation of Au substitutionals in the center of the sample versus the square root of diffusion time.

claim, but reaches $[Au_{si}] = 0$ at finite positive time, which is necessary for Au_i to reach the center of the sample. Secondly, although the longer time data and the shorter time period can be fitted to a line, there is an inflection point that was not reported previously. To some extend, the simulation result is consistent with the result of our laboratory experiments[10].

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