Onset of Interstitial Diffusion Determined by Scanning Tunneling Microscopy

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A new method using variable temperature scanning tunneling microscopy (STM) to determine the onset temperature of the diffusion of self-interstitial atoms is presented. The interstitials are produced by a low fluence of Ne^+ (4.5 keV) bombardment of Pt(111) at 20 K. At 22 K, the interstitials become mobile and migrate to the surface where they pop out and can be detected as new adatoms by STM. The time dependence of the appearance of the interstitials at the surface is measured for two temperatures, allowing estimation of the diffusion parameters. [S0031-9007(97)03823-4]

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The annealing processes of damage produced by ion bombardment have long been a matter of interest. While earlier measurements were mainly focused towards the understanding of ion-wall interactions in nuclear reactors [1], nowadays the interest is mostly directed to the use of ions in processes of material modification and analysis [2]. It appears that a complete understanding of the morphological evolution of the target during the mentioned processes requires a detailed knowledge of the defect morphology of single ion impacts and their annealing. Self-interstitial atoms (briefly interstitials) are usually the most mobile form of defects produced by ion bombardment [1]. Since a knowledge of the lowest temperature annealing process is the base to understand more complex annealing processes, it is desirable to have a widely applicable method to determine the number of interstitials per impact (yield) and their mobility.

To our knowledge, mainly two types of methods have been used to obtain information about interstitials, especially on mobilities. Bulk measurements like the kinetic analysis of annealing curves were mostly used to get quantitative information about interstitial diffusion [1]. Since a homogeneous distribution of interstitials in a thin foil target material is required, bulk measurements have the disadvantage that they are restricted to self-interstitials produced by particles with a relatively large mean free path like electrons and neutrons. Information about the interstitials close to the surface produced by ions in the depth of the order of 100 Å is thus not accessible. However, most ions used in material modification cause radiation damage in this range. The second way to access information about interstitials is a microscopic method and uses field ion microscopy (FIM) [3]. It allows one to investigate the ion impact damage and the mobility of defects produced close to the surface, but, unfortunately, is restricted to a small class of hard materials and a tip shaped target geometry. The latter leads to an extremely large surface to bulk ratio, which might influence the results.

In this paper, we present a new method to determine the onset temperature of self-interstitial diffusion and to estimate the number of interstitials produced per single ion impact. The method is similar to the FIM method [3], but uses the variable temperature scanning tunneling microscope (STM). Thus it is applicable to a larger number of target materials, including most metals and semiconductors. The method determines the onset of interstitial diffusion by the detection of the appearance of the interstitials at the surface. Here, the STM method is applied for interstitials produced by Ne^+ (4.5 keV) impacts on Pt(111).

The experiments were performed in a UHV-STM apparatus described elsewhere [4]. Briefly, a He-flow cryostat is used to cool the sample to 20 K. A filament on the back side of the sample is used to increase the temperature. The background pressure of the apparatus is 5×10^{-11} mbar. The sample temperature is measured by a NiCr-Ni thermocouple calibrated by the multilayer desorption peaks of Ar, Kr, and Xe [5]. The uncertainty in the absolute temperature measurement is ± 2 K at 20 K, but the reproducibility is about ± 0.5 K. The Pt(111) sample was prepared by repeated cycles of Ar^+ (600 eV) ion bombardment and O_2 exposure, both at 720 K, and a subsequent annealing to 1270 K. This results in a clean, well ordered surface. Interstitials are produced by Ne^+ (4.5 keV) ions supplied by a differentially pumped ion gun. The sample temperature during bombardment is ≤ 20 K and the fluence is 1×10^{11} ions/cm^2. STM images of the ion bombarded surface at 20 K and during the annealing of the interstitials at higher temperatures are obtained with a beetle-type STM in the constant current mode at $U = 0.3$ V and $I = 1$ nA. The images are taken every 2 min. All images are shown in the differential mode appearing as illuminated from the left. It was checked that, at the imaging temperatures used, the tunneling process does not influence the damage patterns of the ion impacts. Since the interstitial diffusion takes place below the surface, we suppose that the tunneling process does not influence the interstitial diffusion

either. Finally, at the temperatures used here all surface diffusion processes on Pt(111) are frozen out.

Figure 1(a) shows the Pt(111) surface after Ne^+ (4.5 keV) bombardment at 20 K. The fluence corresponds to 9 ion impacts in the shown surface area of 950 Å × 950 Å. Besides two preexisting steps, a number of white dots are observable in Fig. 1(a). Such white dots do not exist prior to ion bombardment. Counting the number of dots in topographs after the annealing of interstitials at higher temperatures gives an average of 4.0 ± 0.2 white dots related to each Ne^+ (4.5 keV) impact. According to the recipe described in Ref. [6], we also determined the adatom yield—the average number of adatoms created per impact—for Ne^+ (4.5 keV) and obtained a value of 3.8 ± 0.4 [7]. Thus it must be concluded that with a probability close to one a white dot is an isolated adatom and that only a small fraction of the white dots is due to adatom clusters. From now on we identify white dots with single adatoms. In contrast to the situation after annealing of the interstitials, only about three adatoms per impact are observed in Fig. 1(a) as well as in other images obtained at 20 K. This is already a hint that interstitials are not completely annealed at 20 K. Repeated imaging of the same surface area at 20 K does not change the number and position of adatoms in the image. Heating to 22 K leads to the appearance of additional adatoms on the surface as shown in Figs. 1(b)–1(d). (Areas where additional adatoms appear are marked by white circles, and the first appearance of every additional adatom is marked by an arrow.) The number of additional adatoms between two shown images is also noted. The total increase in the number of adatoms in experiments with annealing to 22, 25, and 40 K is always 20%–30%. Since no additional adatoms appear during STM imaging at 20 K and since the ratio of the number of adatoms popping out during annealing to that of adatoms present prior to annealing is the same in all experiments, one tends to attribute the former to migrating interstitials appearing at the surface. To exclude that the additional white dots appearing during annealing are due to adsorbates from the gas phase, we performed a test experiment: the sample is bombarded at 40 K and the temperature is kept at 40 K for 2 min in order to anneal all interstitials. Then the sample is cooled to 20 K and the same annealing experiment as shown in Fig. 1 is performed: The sample is heated again to 22 K and an image is taken every 2 min for a period of 30 min. Not a single additional white dot appears during this period. Thus, the additional white dots found in the experiments after ion bombardment at 20 K are not due to atoms from the residual gas phase adsorbing on the surface, but to interstitials migrating to the surface.

Figure 2(a) presents averaged data of the time dependence of the appearance of the interstitials at the surface. They are obtained from annealing experiments at 22, 25, or 40 K. To ease the comparison, the fraction of additional adatoms with respect to the number of adatoms observed prior to annealing is shown. As mentioned above the total increase in the number of adatoms is always about 20%–30%. Since the adatom yield including annealed interstitials is four, as described above, on average one stable interstitial is produced per Ne^+ (4.5 keV) impact. To be more specific, one has to take into account that only a certain fraction of interstitials created is detected in our experiments. First, all close interstitials which did not escape their corresponding vacancies, i.e., which are still elastically interacting with their vacancies, will not be detected at the surface. As soon as they become mobile, each of these close interstitials will recombine with its vacancy (annealing stages I_A, I_B, and I_C as defined in Ref. [1]). Second, also some of the free interstitials, which escaped the recombination volume around their corresponding vacancy and which correspond to the annealing stages I_D and I_E, may be captured by a vacancy during their thermally activated random walk. However, for a randomly

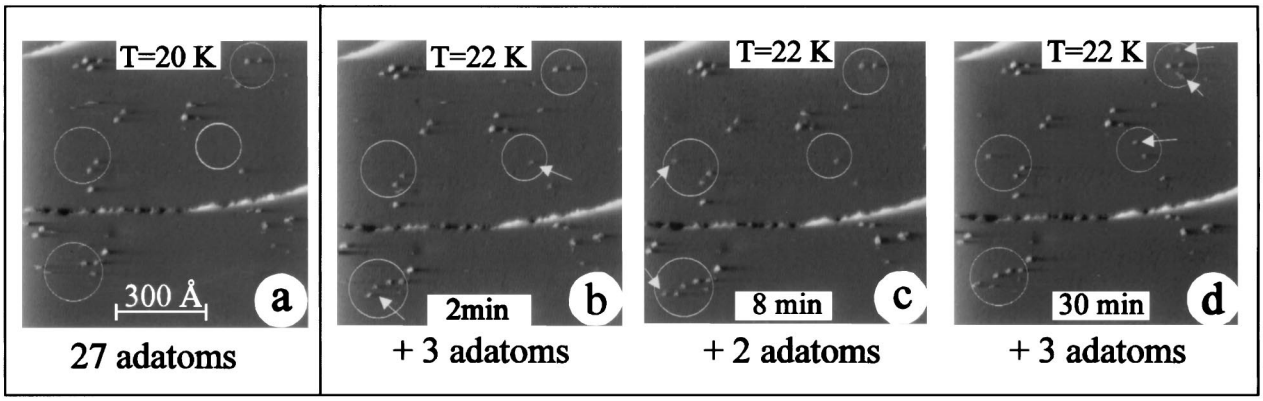

FIG. 1. Appearance of migrating self-interstitial atoms at the surface at 22 K: (a) Pt(111) surface after Ne^+ (4.5 keV) ion bombardment at 20 K, $F = 1 \times 10^{11}$ ions/cm^2 (= 9 impacts/950 Å × 950 Å); (b)–(d) same surface area as in (a), but obtained after keeping the surface at 22 K for 2, 8, and 30 min, respectively. Circles mark the areas where additional adatoms (migrating interstitials) appear, and arrows show their first appearance. The time at the annealing temperature and the number of additional adatoms between two shown images are indicated. ($U = 0.3$ V, $I = 1$ nA.)

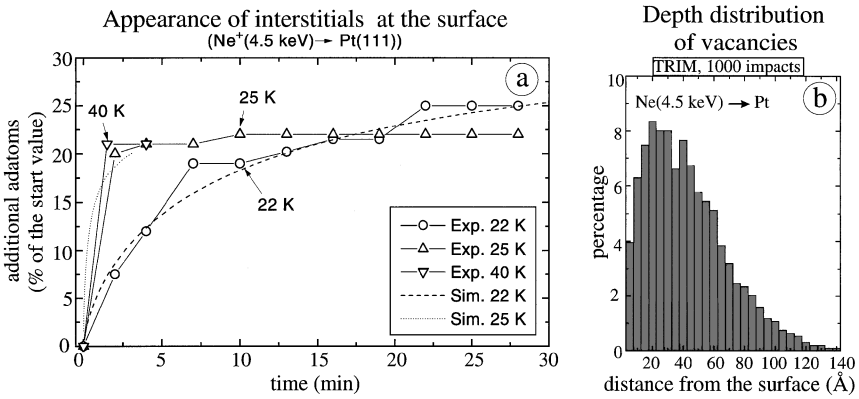

FIG. 2. (a) Time dependence of the appearance of interstitials at the surface at different temperatures. Symbols are experimental values which are connected by full lines. Dashed and dotted curves (Sim.) are calculated fits (see text). (b) Depth distribution of vacancies calculated with TRIM [9]. The distribution is used as the starting depth distribution of the self-interstitial atoms for the simulated curves shown in (a) (see text).

migrating interstitial the surface is an extremely large sink compared to the available bulk vacancies. Therefore the probability of a free interstitial to anneal at the surface will be larger than to get captured by a vacancy. Third, since the bombardment temperature is close to the onset temperature of diffusion of free interstitials, interstitials produced very close to the surface might already pop out during the bombardment at 20 K. Because of an elastic interaction with the surface, such interstitials could become mobile at lower temperatures than interstitials in the bulk. If during bombardment the temperature of the sample can be lowered sufficiently, there is in principle no restriction to detect these close-to-surface interstitials—if existent—as well. In conclusion, the detected number of one interstitial per Ne^+ (4.5 keV) impact is a lower limit of the yield of freely migrating interstitials created.

From the shape of the curves in Fig. 2(a), one infers that, as expected for an Arrhenius behavior of self-interstitial diffusion, the annealing is faster at higher temperatures. To estimate the diffusion energy E_D and the prefactor ν_0 from Fig. 2(a), one has to assume a depth distribution of the *interstitials* prior to annealing. In the absence of better information we used TRIM [8] to calculate the depth distribution of *vacancies* created in an amorphous Pt target [Fig. 2(b)]. This depth distribution of vacancies, shown in Fig. 2(b), is taken as the depth distribution of interstitials.

It is used as the starting distribution of the interstitials, called $P(n, t = 0)$ with n being the nth layer from the surface and t being the annealing time at a given temperature. A simple one dimensional model is able to reproduce the time dependence of the appearance of interstitials at the surface. Jumps in the direction perpendicular to the surface are described as a Markov chain with one absorbing end, the surface [9]. The number of jumps N necessary for a certain fraction of interstitials to reach the surface is calculated by considering the possible paths reaching the surface after N_n jumps with n being the starting layer. This results in an expression for the probability $P(N_n)$ that an interstitial from layer n reaches the surface after N jumps. Values for the expression for different N and n are calculated numerically. The fraction of interstitials having reached the surface ($n = 0$) after N jumps is then

$$P(n = 0, t = t(N)) = \sum_n P(N_n) P(n, t = 0) .$$

The next step is to identify the number of jumps N with the experimental time t by using the diffusion parameters E_D and ν_0 in the usual Arrhenius form. One has to take into account that the real interstitial diffusion is three dimensional and that, as can be checked geometrically, only $\frac{6}{12}$ of the interstitial jumps lead to a layer change. (Only jumps between $\langle 100 \rangle$ dumbbell configurations are considered [1].) This leads to

$$N(t) = \frac{6}{12} \nu_0 t \exp\left(-\frac{E_D}{kT}\right) .$$

T is the temperature, and k is the Boltzmann factor. Taking the diffusion parameters as fitting parameters, the curves in Fig. 2(a) are reproduced. The best fit is found for $E_D = 50$ meV and $\nu_0 = 6 \times 10^{11}$ s^{-1} and the corresponding calculated curves (Sim.) are drawn in Fig. 2(a) as dashed (22 K) and dotted (25 K) lines.

In these experiments, the main error in the determination of E_D and thus of ν_0 is the uncertainty of the absolute sample temperature ($\pm 10\%$). The other errors, in particular, the statistical error of the data, the variance of the fitting procedure, and the uncertainty in the starting depth distribution of the interstitials are of minor importance such that the overall E_D error can be estimated to be about $\pm 12\%$. The values obtained above are in reasonable agreement with data from the only macroscopic bulk experiments conducted so far in which $E_D = 60$–70 meV and $\nu_0 = 9 \times 10^{11}$ s^{-1} have been measured for Pt [10].

In conclusion, we have demonstrated a new microscopic method to determine the onset of interstitial diffusion,

which allows one to estimate the interstitial diffusion parameters and the interstitial yield. The method is applicable to most metals and semiconductors. Importantly, it is possible to investigate the number and diffusion of interstitials produced close to the surface. For Ne^+ (4.5 keV) ion impacts on Pt(111) it is found that a single impact produces on average at least one freely migrating interstitial. The diffusion parameters of interstitial migration were determined with the help of a one dimensional model of diffusion to be $E_D = 50 \pm 6$ meV and $\nu_0 \approx 6 \times 10^{11}$ s^{-1} in reasonable agreement with previous data determined from resistance annealing curves.

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