Binding and Mobility of Isolated Indium Atoms on Si(111)7×7

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PAC spectroscopy has been used to study diffusion and desorption of isolated ^{111}In atoms adsorbed on a Si(111)7×7 surface. Two different adsorption sites are found and their hyperfine parameters are determined as a function of temperature and compared to first-principles calculations. The activation energy for the migration to regular adsorption sites is determined to be 0.72(5) eV. The relative population of the two adsorption sites changes at about 500 K corresponding to an activation energy of 1.61(15) eV for this process. The binding energy of the indium atoms is estimated to be 1.93(10) eV. The desorption behavior is found to be strongly dependent on In concentration in the low coverage regime.

In recent years, the use of hyperfine techniques has been established as an advantageous complementary approach to study surface, interface, and thin-film phenomena by local probes [1]. In particular, the perturbed $\gamma\gamma$ angular correlation (PAC) method has proven to be a quite powerful technique, since the rather small number of radioactive probe nuclei needed for the experiment does not significantly disturb the system under consideration. Using the electric-field gradient as a characteristic measure for the lattice site occupied by the probe atoms, the technique has been used to study problems like surface diffusion [2], surface [3] and thin-film magnetism [4], as well as interface compound formation [5] on microscopic scales. However, while a large number of PAC studies have been performed to investigate bulk semiconductor properties [6], surface and interface PAC experiments have so far been restricted to metal surfaces only. This is in contrast to the great interest in semiconductor surfaces and metal/semiconductor interfaces which has developed over the last two decades mainly because of the outstanding technological relevance.

In this Letter we report on a first application of the PAC method to study the diffusion and desorption behavior of isolated ^{111}In atoms on a free semiconductor surface. The system In/Si(111) has been chosen since it has been studied in the past by various surface-sensitive techniques and a quite comprehensive picture has developed on the adsorption behavior of submonolayer indium films. Since the pioneering work by Lander and Morrison [7], a complete two-dimensional phase diagram has been established mainly by low-energy electron diffraction (LEED) [8] and reflection high-energy electron diffraction (RHEED) [9] experiments; recent investigations using scanning tunneling microscopy (STM) have led to additional information on the adsorption geometries in the various indium superstructures [10,11]. The desorption behavior has been studied as well by RHEED [12] yielding different desorption energies for the various In superstructures. However, due to sensitivity limitations of the conventional surface techniques, all studies reported so

far have been restricted to indium concentrations above typically 0.01 ML. Here, the use of radioactive probe nuclei gives access to a wider range of adsorbate concentrations down to a minimum of about 10^{-4} ML. Moreover, monitoring the total radioactivity of the sample provides a straightforward means to study desorption processes with high accuracy.

The radioactive isotope ^{111}In is a well-suited PAC probe; it decays through electron capture to an excited nuclear state of ^{111}Cd, which in turn is depopulated through the emission of two γ quanta to the ground state of ^{111}Cd. The isomeric $I = \frac{5}{2}$ state of ^{111}Cd ($T_{1/2} = 84$ ns), intermediate in this $\gamma\gamma$ cascade, may be split by the interaction of its electric quadrupole moment ($Q = 0.83$ b) with an extranuclear electric-field gradient. This leads to a characteristic time dependence of the coincidence counting rate of the two γ quanta. Conventionally a counting rate ratio $R(t)$ is formed from different coincidence spectra, essentially containing the superposition of harmonic oscillations of the transition frequencies ω_1, ω_2, and $\omega_3 = \omega_1 + \omega_2$ between the sublevels of the isomeric state. From these frequencies the strength V_{zz} and asymmetry $\eta = (V_{yy} - V_{xx})/V_{zz}$ of the electric-field gradient tensor are obtained; the orientation of the field gradient principal-axis system is reflected in the relative amplitudes of the three transition frequencies in the $R(t)$ time spectra. (For a detailed description of the method, refer to Ref. [13].)

For the present experiments, a (111)-oriented Si wafer has been mechanically polished to mirror finish and then degreased and etched following standard procedures. After some outgassing in UHV the crystal has been flashed several times to about 1200 °C by electron bombardment in order to remove the native oxide layer. After cooling to room temperature, a bright (7×7) pattern could be detected by LEED. Auger electron spectra showed no residual contaminants within a detection limit of 0.005 ML (for carbon). For the PAC experiments about 10^{-4} ML of the radioactive isotope ^{111}In has been deposited onto the surface at different substrate tempera-
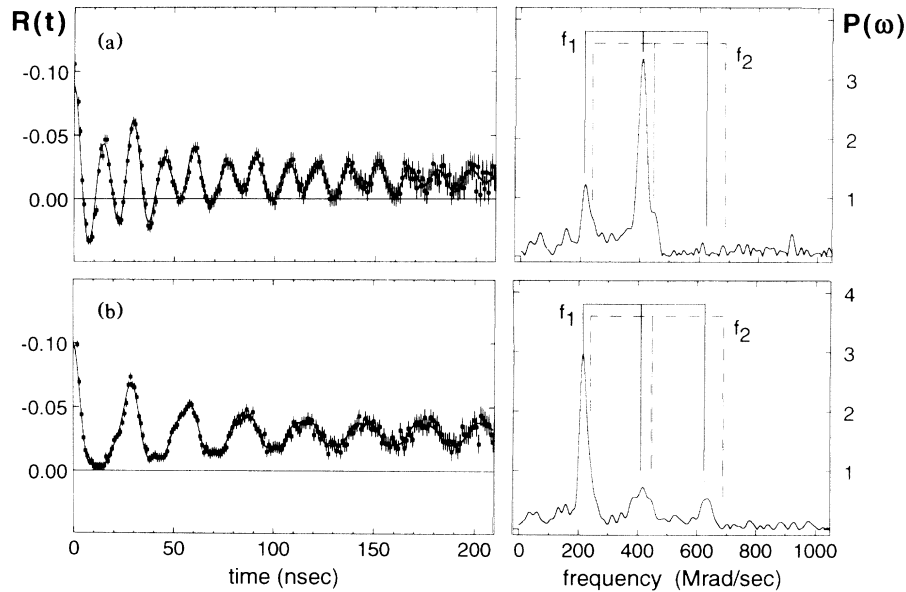
FIG. 1. PAC time spectra and corresponding Fourier transforms for ^{111}In on Si(111)7×7 for two different sample-detector geometries: (a) The surface normal within the γ detector plane pointing under 45° between two adjacent γ detectors; (b) the surface normal tilted by 80° with respect to the detector plane. The solid lines indicate least-squares fits to the data.

tures.

In a first series of experiments, the probe atoms have been deposited onto the Si(111)7×7 surface at room temperature and the sample has been subsequently annealed to 550 K for 10 min. PAC time spectra have then been recorded at room temperature. Figure 1 shows two $R(t)$ time spectra and corresponding Fourier transforms for two different sample-detector geometries. A least-squares fit to the time spectra reveals that a dominant fraction f_1 of the probe atoms experience a rather unique and strong electric-field gradient [$V_{zz} = 1.09(12) \times 10^{18}$ V/cm^2] of almost axial symmetry [$\eta = 0.20(3)$]. From the variation of the Fourier amplitudes as a function of sample-detector geometry the direction of the z-principal axis of the field gradient tensor is found to be perpendicular to the (111) surface plane. As can be seen as a shoulder in the Fourier spectra, a small fraction f_2 of about 10% of the probes are exposed to a slightly higher electric-field gradient [$V_{zz} = 1.25(15) \times 10^{18}$ V/cm^2; $\eta = 0.25(4)$] of almost the same symmetry and orientation. The hyperfine fields have then been studied as a function of measurement temperature between 100 and 400 K. While symmetry and orientation of the electric-field gradient tensors are found to be temperature independent, the strengths V_{zz} of the hyperfine fields increase slightly as the measurement temperature is decreased. The data are well represented by a linear temperature dependence $V_{zz}(T) = V_{zz}(T=0)(1-BT)$, yielding the linear coefficients listed in Table I. It is worth mentioning that the strength B of the temperature dependence is found to be the same for both field gradients; this is an indication of a quite similar adsorption geometry for either probe site.

For a microscopic probe-site determination it is instructive to compare the above results with data obtained for the lowest concentrations accessible in conventional surface-sensitive experiments. It has been shown by electron diffraction [8,9] that an indium coverage up to about 0.3 ML preserves the (7×7) reconstruction, only leading to changes in the relative intensities of the superstructure diffraction spots. Recent STM investigations of the low-concentration regime indicate that indium atoms replace Si adatoms in the unit mesh of the (7×7) reconstruction [11], as described by the dimer–adatom–stacking-fault (DAS) model [14] (see Fig. 2). Moreover, after deposition at about 700 K the indium atoms were found to preferentially occupy adatom sites near the edges of the (7×7) unit cell rather than corner sites. This finding was attributed to slight differences in the binding energy be-

TABLE I. Electric-field gradient parameters for ^{111}In/^{111}Cd on Si(111)7×7. The parameters are obtained by a least-squares fit to the experimental data according to the relation $V_{zz}(T) = V_{zz}(0)(1-BT)$.

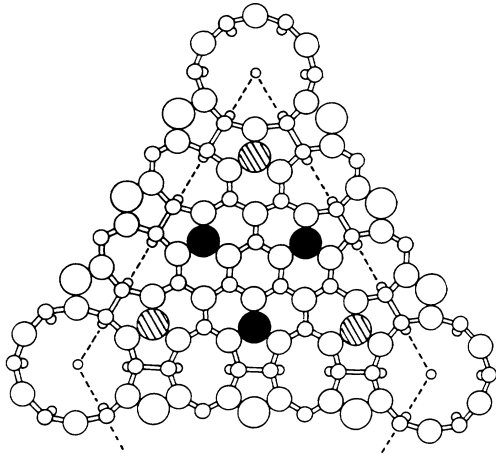| Probe site	$V_{zz}(T=0 \text{ K})$ (10^{18} V/cm^2)	η	B (10^{-4} K^{-1})
	Experiment (this work)		
f_1	1.20(12)	0.20(3)	2.81(4)
f_2	1.37(15)	0.25(4)	2.82(5)
	Theory (Ref. [15])		
Eclipsed	1.41	0	$\cdots$
Atop	2.12	0	$\cdots$

FIG. 2. Part of the (7×7) unit cell according to the DAS model [14]. The first four Si layers are shown by open circles of successively decreasing size. Possible indium sites are indicated by solid circles (f_1, edge site) and hatched circles (f_2, corner site).

FIG. 3. (a) The fractions f_1 and f_2 of ^{111}In probe atoms exposed to the two different field-gradient situations as a function of annealing temperature. The solid lines are guides to the eye. (b) The fraction of desorbed ^{111}In probe atoms as a function of annealing temperature. Solid circles: Isolated ^{111}In on Si(111)7×7. Open squares: 10^{-4} ML ^{111}In plus 0.05 ML natural indium.

tween both sites. This model is perfectly confirmed by the PAC results described above. Two different adsorption sites are observed with quite similar electric-field gradients and an almost equal temperature dependence of the hyperfine fields. After annealing to 550 K site f_1 is preferentially populated; the relative occupation between f_1 and f_2 amounts to about 5:1 and compares well with a relative occupation for edge to corner sites of 6:1 reported to Ref. [11] for deposition at 700 K. We therefore identify f_1 as the fraction of ^{111}In probes occupying adatom positions at the edges of the (7×7) unit cell (Fig. 2, solid circles) while the fraction f_2 corresponds to ^{111}In atoms on adatom positions near the (7×7) corner holes (Fig. 2, hatched circles).

This interpretation is independently confirmed by a recent theoretical work by Mohapatra et al. [15], who predicted the electric-field gradient for ^{111}In/^{111}Cd on different adsorption sites on Si(111). This work is based on first-principles molecular cluster calculations which have been used quite successfully in the past to determine the hyperfine fields for isolated ^{111}In/^{111}Cd atoms on metal surfaces [16]. For the system ^{111}In/^{111}Cd on Si(111) two different adsorption sites are taken into consideration, an eclipsed position corresponding to the adatom site discussed above, and an atop position with the indium atom residing on top of a single silicon surface atom. The results of these calculations are included in Table I. Since no lattice vibrations are taken into account, these results should compare to the experimental values extrapolated to $T=0$ K. Although the experimental results differ by about 15% from the theoretical prediction, they clearly favor eclipsedlike indium adsorption geometries for both indium sites observed in the PAC experiments. While a vanishing asymmetry parameter is predicted by theory due to the threefold symmetry of the cluster used for the
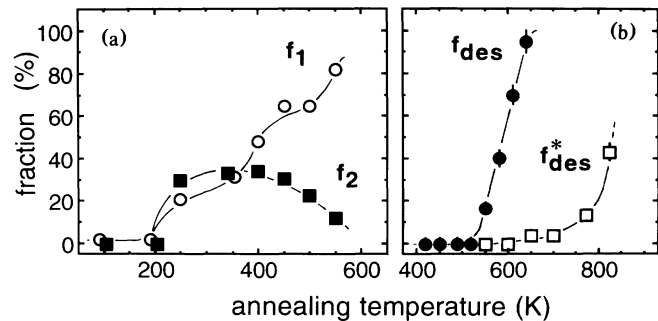
calculations, a small asymmetry of the electric-field gradient is observed in the experiment. This is explained by the arrangement of next-nearest neighbors of the adatom positions in the (7×7) unit cell. The fact that two slightly different electric-field gradients are observed may be also due to differences in the second shell of nearest-neighbor atoms for the adatoms in edge and corner positions, respectively.

In order to gain insight into the mobility of the indium atoms on the surface, additional experiments were performed where the radioactive probes were deposited onto the Si(111) surface at 100 K. PAC spectra were then recorded at 100 K after isochronically annealing the sample to successively increasing temperatures. Figure 3(a) shows the fractions f_1 and f_2 of probe atoms experiencing the two different field gradients as a function of annealing temperature [17]. As can be seen from the figure, at about 225 K the indium atoms become mobile enough to move from different adsorption sites randomly occupied at 100 K to unique adsorption sites characterized by well-defined hyperfine fields. Assuming a thermally driven diffusion process following an Arrhenius-type behavior we deduce an activation energy of $E_A=0.72(5)$ eV for this first diffusion step [18]. At room temperature both sites are populated to about the same amount; however, at annealing temperatures above 500 K probe site f_2 is depopulated in favor of f_1. From the conversion temperature an activation energy of $E_A(f_2 \rightarrow f_1)=1.61(15)$ eV can be estimated.

The desorption behavior of the indium atoms has finally been investigated by monitoring the total radioactivity of the sample as a function of annealing temperature. As can be seen from Fig. 3(b), already at 600 K a considerable fraction of the probes has desorbed from the surface. Assuming an attempt frequency of 10^{13} Hz [12], this corresponds to a binding energy of $E_B=1.93(10)$ eV. This value is rather low as compared to an earlier work by

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Baba, Kawaji, and Kinbara [12], who studied isothermal In desorption from In superstructures formed on Si(111) at higher In concentrations. From this work a significantly higher desorption energy $E_B = 2.73(8)$ eV is reported for an In coverage of 0.3 ML.

To check our results on the desorption behavior, additional PAC experiments were performed where about 0.05 ML of natural indium was added to the radioactive probes. The hyperfine parameters are essentially the same as found for the isolated indium probes discussed above, indicating that there is no difference in the adsorption geometry as compared to the isolated probe atoms discussed above. However, the desorption temperature is found to be drastically shifted to higher values as the indium concentration is increased. This has been additionally indicated in Fig. 3(b). From the data a lower limit of the desorption energy may be estimated as $E_B > 2.6$ eV for the higher indium concentration. This is in good agreement with the results from Ref. [12]. We therefore conclude that the binding energy increases with increasing indium concentration, while no change in the adsorption geometry is observed.

In summary, we have demonstrated the applicability of the PAC technique to study isolated adsorbates on semiconductor surfaces down to extremely low concentrations. Strong and unique electric-field gradients have been found and could be attributed to probe atoms substituting Si adatoms within the unit mesh of the Si(111)7×7 surface. The strength of the hyperfine fields compares well to theoretical predictions. Isochronal annealing cycles provided insight into both the mobility and the desorption behavior of the indium atoms. The fact that PAC allows one to determine the probe site and mobility of highly diluted local probes on semiconductor surfaces certainly opens a wide field of further applications, in particular for the study of metal/semiconductor interfaces and multilayers.

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[18] For the attempt frequency the result of Ref. [12] has been taken, $\nu_0 = 3 \times 10^{14}$ Hz.