Soft-Landing Ion Deposition of Isolated Radioactive Probe Atoms on Surfaces: A Novel Method

C. R. Laurens,* M. F. Roşu, F. Pleiter, and L. Niesen
Nuclear Solid State Physics, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 13 February 1997)

We present a method to deposit a wide range of radioactive probe atoms on surfaces, without introducing lattice damage or contaminating the surface with other elements or isotopes. In this method, the probe atoms are mass separated using an isotope separator, decelerated to 5 eV, and directly deposited on the surface. The method allows for performing hyperfine interactions experiments using trace amounts of radioactive probes located at surfaces and interfaces. The characteristics of the deposition method were studied by performing perturbed angular correlation experiments on the system In on Cu(17,1,1). The results are in agreement with molecular dynamics simulations of the deposition process. The potential of this novel technique is briefly discussed. [S0031-9007(97)03222-5]

PACS numbers: 68.35.Dv, 76.80.+y

In the past several years, perturbed angular correlation (PAC) spectroscopy on radioactive probes has proved to be a powerful method in the study of surface phenomena. Topics like surface diffusion, surface roughening, and surface magnetism have been addressed in a number of publications [1–4]. However, an important technical difficulty in the successful application of hyperfine interaction techniques is the clean deposition of the radioactive probe atoms onto the surface. This is especially true because the necessary isotopes are generally not available in a pure form. Over the past several years a few methods have been developed for separating radioactive probe atoms from the source material. In the following we briefly discuss their characteristics.

The Konstanz group developed a physiochemical separation procedure to extract the frequently used probe ^{111}In from a ^{111}InCl$_3$(HCl) solution [1]. The method relies on the different sticking factors of indium and chlorine to particular substrates. By using a multistep evaporation process with two intermediate substrates, the Konstanz group succeeded, over the years, to reduce the predominant chlorine contamination on the final substrate from 10% to 2% of a monolayer, in the most favorable cases. Although the method can be adapted to other isotopes than ^{111}In, careful optimalization in choosing the intermediate substrates and evaporation temperatures is needed for every single element. Furthermore, the method is unable to separate different isotopes of the same element, which is essential in the application of ^{100}Pd [5]. The method also appears to be rather inefficient: out of 200 MBq of ^{111}InCl$_3$ typically one to two samples are produced, each with a source strength of approximately 200 kBq.

An alternative separation method was developed by the ISOLDE group at CERN [4]. Here, the available isotope separator is used to extract the desired probe atoms, which are then implanted in a precleaned target. The probes are subsequently diffused out by heating and evaporated on an intermediate substrate, from which they are evaporated on the surface under study. Obviously, the method is capable to adequately separate the wanted isotope from the source material. However, similar remarks can be made regarding the necessary intermediate substrates and the material efficiency.

The deposition method presented in this Letter is designed to overcome the previously mentioned limitations. As at ISOLDE, we employ an isotope separator to produce an isotopically pure ion beam of the radioactive probe atoms, which are transported via a differentially pumped beam line to a UHV chamber. There the ions are decelerated to an energy of approximately 5 eV and *directly* deposited on the surface. Since no intermediate substrates are used, contamination of the surface by other elements can be much better controlled. To characterize the deposition method, we chose the model system In on Cu(17,1,1). This system has been studied previously by Fink *et al.* [1] using perturbed angular correlation spectroscopy and by Breeman using low energy ion scattering [6] and computer simulations [7]. In this Letter we present the results of our perturbed angular correlation studies and molecular dynamics (MD) simulations. The technical aspects of the soft-landing deposition method will be discussed in a second paper [8].

A Cu single crystal was mechanically polished parallel to the (17,1,1) plane with an accuracy of better than 0.1°, and subsequently chemically etched. The samples were cleaned *in situ* by a few cycles of sputtering with 1 keV Ar$^+$ followed by annealing at 600 K for 2 h. Low-energy electron diffraction showed the expected terraces with a length of 8.5 interatomic distances, and monoatomic steps. Indium atoms were deposited with an energy of approximately 5 eV to a dose of 10^{12} cm^{-2}, at a substrate temperature of 80 K. At these low temperatures, thermally activated diffusion for both In and Cu adatoms is inhibited [6]. The $\gamma\gamma$-coincidence count rates were measured using a standard four-detector slow-fast setup. The [100] crystallographic direction was oriented in the detector plane at angles of 45° and 135° relative to the detector axes, while the [011] step direction was oriented perpendicular

0031-9007/97/78(21)/4075(4)$10.00

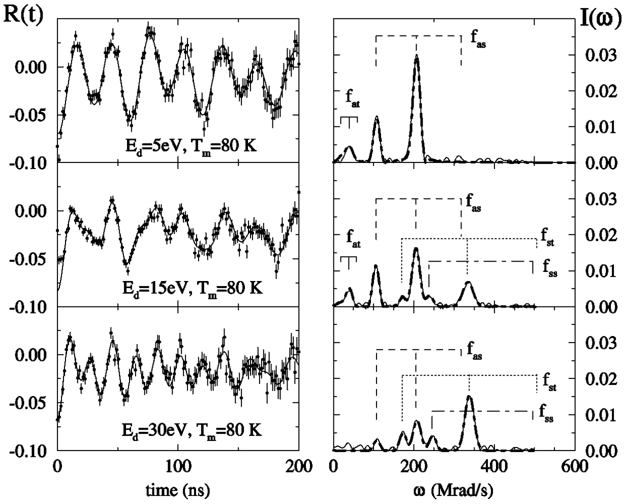

FIG. 1. Typical PAC spectra after the soft-landing deposition of ^{111}In probes at energies of 5, 15, and 30 eV, respectively, together with their Fourier transforms. The characteristic frequencies corresponding to the different atomic sites are labeled in the Fourier spectra. Note that the second harmonic is suppressed due to the orientation of the crystal with respect to the detectors.

to the detector plane. In Fig. 1, typical PAC spectra are shown together with their Fourier transforms, which were obtained after deposition of the ^{111}In probes at energies of 5, 15, and 30 eV, respectively.

After deposition of indium probes with an energy of 5 eV, two well defined sites are observed, labeled f_{at} and f_{as} in Fig. 1. The hyperfine parameters belonging to these sites are identical to those previously observed after vapor deposition of the probes at 80 K, and have been attributed by Fink *et al.* [1,9] to indium atoms occupying adatomic terrace sites and adatomic step sites, respectively. Thus at this energy the indium atoms are found only at sites on top of the surface. Since the hyperfine parameters are very well defined and closely match those found after evaporation of the indium probes, we conclude that the lattice was not damaged at the indium probe sites. It is striking that almost 90% of the indium atoms are located at copper step edges. This might indicate that directly after deposition the In atoms are able to move over the surface due to their excess transverse kinetic energy.

After deposition of indium probes with an energy of 15 eV, two additional sites appear, labeled f_{st} and f_{ss} in Fig. 1. The site f_{st} has previously been observed only after annealing at approximately 300 K, and was interpreted by Fink *et al.* [1] as being the substitutional terrace site. Apparently, the indium atom is now able to displace a surface copper atom from its lattice position and occupy the created vacancy. From the analysis of the data we conclude that the copper atom is most likely displaced to at least a next-nearest neighbor position. The site f_{ss}, with hyperfine parameters $\nu_Q = 148(1)$ MHz and $\eta = 1.00(5)$ has not been reported so far, although the parameters are comparable to that of a site f_x interpreted by Fink *et al.* [3] as being the substitutional step site. We have good reasons to believe that the currently reported site corresponds to the substitutional step site. First, we found that the anneal behavior of the f_{ss} site was similar to that reported by Fink *et al.* for the f_x site and also similar to the behavior of the substitutional step site of In on Ag(17,1,1) [1]. Second, in a study of In on Ag(17,1,1) also an η value of 1.0 has been reported for the substitutional step site [1].

After deposition of indium probes with an energy of 30 eV a new contribution to the PAC spectrum was found, which had not been found in the evaporation experiments of Fink *et al.* [5,6]. The corresponding indium atoms are located in a cubic symmetric environment and give rise to a constant offset in the PAC spectra. We suggest that this site is related to substitutional lattice sites in deeper layers.

In Fig. 2(a), we plotted the occupation of the different sites as a function of the deposition energy, as derived from our PAC data. For the sake of presentation the observed sites are combined into three groups: top layer sites (adatomic terrace and adatomic step), first layer sites (substitutional terrace and substitutional step), and

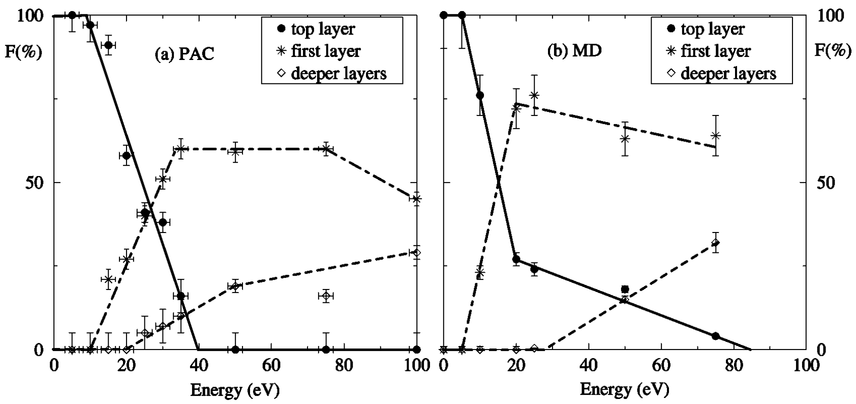

FIG. 2. The In-site occupation as a function of energy as derived from the PAC experiments (a) and the MD simulations (b). The occupation as derived from the PAC data has been renormalized to the maximum visible fraction in this series of experiments.

deeper layer sites (cubic symmetric site). It turns out that these sites account for about 55% of the deposited In atoms, depending on the experimental conditions. The remaining fraction of the In atoms appears to be subject to a distribution of hyperfine interactions, which results in a fast damping of the associated modulation amplitude in the PAC spectrum. It should be noted that Fink *et al.* [1] reported a visible fraction of approximately 60% for ^{111}In atoms evaporated on vicinal Ag(100). Because of the fact that a large area of the crystal surface is sampled in a PAC experiment, we speculate that the visible fraction is related to the quality of the surface after preparation of the crystal rather than to the deposition method.

In order to corroborate the interpretation of our PAC data, we performed molecular dynamics simulations of the deposition of In on a Cu(100) surface. We used the atom-embedding model of Finnis and Sinclair (FS) [10] to describe the interatomic interactions. For the Cu-Cu potential, we used a modified FS potential proposed by Foreman [11]. Compared to the original Ackland potential [12], the modified FS potential has a much steeper repulsive interaction, which is necessary to correctly reproduce the anisotropic displacement energies in fcc copper. For the In-Cu potential we modified the potential originally constructed by Breeman [7] in an analogous way. To our knowledge no experimental data are available for the anisotropic displacement energies in InCu alloys. Therefore, we used a Hartree-Fock-Slater approach to calculate the energy of an In-Cu pair at distances between 0 and 3 Å. The result was augmented to the original potential, using a third-order Taylor expansion around the equilibrium position.

The Cu(100) surface was represented by a slab consisting of 16 layers with 256 atoms per layer, and with periodic boundary conditions parallel to the surface. The atoms in the three bottom layers were kept fixed at their equilibrium positions so that they served as a structural template, whereas the other atoms were free to move. The equations of motion were numerically integrated using the algorithm of Verlet [13]. The temperature of the surface was kept constant by rescaling the velocities of the atoms in the seven layers above the structural template, using a scheme proposed by Berendsen [14].

Simulations were performed for deposition energies from 5 to 75 eV. The In atoms were released at a height of 5 Å above the top layer, at random transverse positions, and with impact angles from 0° to 90° relative to the surface normal. Before every deposition a fresh Cu lattice was generated by thermalizing the initial lattice of the previous simulation for 200 fs. After the deposition the system was followed for 3 to 4 ps, depending on the deposition energy.

From the results of the simulations we obtain the following description of the deposition process. At deposition energies smaller than 6 eV, the In atoms are unable to displace any Cu atoms from their lattice positions. Since the indium atom does not channel into the crystal nor backscatter into the vacuum, it is thus accommodated at a regular adatom site. At incoming angles up to 40° with the surface normal, these adatomic sites are within one or two lattice spacings from the point of impact. However, at larger incoming angles, the indium atoms can travel up to 30 lattice spacings before coming to rest. At deposition energies between 6 and 20 eV, the exchange mechanism becomes the competitive process: an In atom kicks out a Cu atom and occupies the created surface vacancy, while the Cu atom, in turn, is being accommodated somewhere on the surface. At deposition energies larger than 20 eV the indium atoms have sufficient energy to produce Cu interstitial atoms, so that they can penetrate into deeper layers.

To directly compare the results of simulations and experiment, we calculated the energy dependence of the In site occupation from the MD data. As can be seen from Figs. 2(a) and 2(b), the agreement between the results of PAC and MD is remarkably good considering the fact that fairly simple interatomic potentials were used.

In conclusion, we have shown that it is feasible to deposit an isotopically clean beam of In ions on a Cu substrate without introducing lattice damage. Moreover, the atomic sites of the indium probes after deposition at different energies can be successfully predicted by MD simulations.

The soft-landing deposition method is equally well suited for any isotope that can be handled in our isotope separator. It is, for instance, possible to perform Mössbauer spectroscopy on radioactive probes like ^{57}Co. Using radioactive Mössbauer probe atoms on a surface instead of their stable counterparts has the advantage of reducing either the probe concentration or the measuring time by at least a factor of 100.

When this deposition method is combined with molecular-beam epitaxy (MBE), it becomes possible to incorporate probe atoms at well defined sites in thin film structures. This possibility is not only exciting for studies with radioactive probe atoms but is interesting for stable isotopes as well. One could, for instance, study the behavior of dilute concentrations of impurity atoms at metal-semiconductor interfaces, with electrical techniques. In order to explore these possibilities, we currently construct a LN$_2$-cooled transport system which connects the soft-landing UHV chamber and a UHV-MBE chamber.

The technical assistance of L. Venema is highly appreciated. This work was performed as part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

---

*Electronic address: c.r.laurens@phys.rug.nl

[1] R. Fink, R. Wesche, T. Klas, G. Krausch, R. Platzer, J. Voigt, U. Wöhrmann, and G. Schatz, Surf. Sci. **225**, 331 (1990).

[2] J. Voigt, X. L. Ding, R. Fink, G. Krausch, B. Luckscheiter, R. Platzer, U. Wöhrmann, and G. Schatz, Phys. Rev. Lett. **66**, 3199 (1991).

[3] R. Fink, G. Krausch, R. Platzer, U. Wöhrmann, and G. Schatz, Phys. Rev. Lett. **70**, 2455 (1993).

[4] H. Granzer, H.H. Bertschat, H. Haas, W.-D. Zeitz, J. Lohmüller, and G. Schatz, Phys. Rev. Lett. **77**, 4261 (1996).

[5] S. Seeger, H. Haas, and A. Mayer, Hyperfine Interact. **84**, 211 (1994).

[6] M. Breeman and D. O. Boerma, Phys. Rev. B **46**, 1703 (1992).

[7] M. Breeman and D. O. Boerma, Surf. Sci. **287**/**288**, 881 (1993).

[8] C. R. Laurens, L. Venema, G. Kemerink, and L. Niesen (to be published).

[9] R. Fink, K. Jacobs, G. Krausch, J. Lohmüller, B. Luckscheiter, A. Mayer, R. Platzer, B.-U. Runge, U. Wöhrmann, and G. Schatz (unpublished).

[10] M.W. Finnis and J.E. Sinclair, Philos. Mag. A **50**, 45 (1984).

[11] A. J. E. Foreman, C. A. English, and W. J. Phythian, AEA Technology Harwell Report No. AEA-TRS-2028, 1991.

[12] G.J. Ackland, G. Tichy, V. Vitek, and M. W. Finnis, Philos. Mag. A **56**, 735 (1987).

[13] L. Verlet, Phys. Rev. **159**, 98 (1967).

[14] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, J. Chem. Phys. **81**, 3684 (1984).