MOLECULAR DYNAMICS STUDIES OF THIN-FILMS OF Sn ON Cu *

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ABSTRACT

Using Molecular Dynamics, the evolution dynamics of Sn on the (111) and (100) surfaces of Cu have been investigated as a function of coverage and temperature. The interaction potentials are described by modified embedded atom method (MEAM) potentials. The calculated diffusion activation energies of Cu in Sn and Sn in Cu agree reasonably well with experimental values. We find that the structure of the overlayer depends on the morphology of the substrate and remains stable up to temperatures of the order of 75% of the melting temperature of the substrate at which diffusion of Sn into the substrate and Cu atoms onto the overlayer is observed.

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INTRODUCTION

DTIC QUALITY INSPECTED

The dynamical behavior of atoms at an interface is expected to be very different from those in the bulk or at a free surface. In many cases, the interdiffusion of a thin metallic overlayer with a metallic substrate has not been characterized and the structure and composition of the interdiffused layers are not known [1]. Experiments of ultrathin-films of Sn evaporated on a Cu(111) substrate have reported the formation of a stable two dimensional alloy phase with a $p(\sqrt{3} \times \sqrt{3}) - R30^\circ$ structure [2]. This phase is said to form by rapid dissolution of excess Sn into the bulk. Annealing at temperatures as high as 1000 K indicated a loss of the Sn concentration at the surface which is said to become lost to the bulk. The diffusion of Sn into the substrate is surprising because Sn and Cu have very different melting points and at the melting point of Sn (510 K), diffusion of Sn into Cu which occurs via vacancy formation should be negligible when compared to the diffusion of Cu into the Sn which occurs via an interstitial mechanism with small activation energies [3]. Low energy electron diffraction (LEED) studies of thin films of Sn on Cu(100) have found evidence of formation of a commensurate two-dimensional phase with a structure strongly-dependent on anneal temperature and Sn concentration [4]. An earlier study of deposition of Sn on Cu(100) reported no evidence of alloy formation for depositions up to one monolayer (ML) of Sn [5]. Thus, although the study of thin overlayers on Sn on Cu surfaces has helped understand the kinetics and early stages of Cu-Sn alloys formation, there remain many questions in regard to the mobility of Cu and Sn atoms at the interface. For instance, one should expect that for coverages of less than 1 ML, the diffusion of Cu atoms onto the Sn overlayer should be less than the dilute alloy value due to the large reduction in the number of interstitial sites available to the Cu atoms.

We present here preliminary results of Molecular Dynamics (MD) simulations of Sn overlayers on Cu(100) and Cu(111) surfaces. We looked at Sn coverages of up to 2 ML over a wide temperature range: 500-1300 K. Our initial aim was to investigate the kinetics of Sn-Cu alloy formation and to see whether coverages below 1 ML modify the diffusion of Cu atoms into the overlayer via the same interstitial mechanism which occurs in bulk. The atomic interactions are described by modified embedded atoms method (MEAM) potentials [6]. The MEAM formalism is a modification of the well-known embedded atom method (EAM) and includes the angular dependence of the electron density in order to describe bond bending forces necessary to model covalent materials. It has been applied successfully to fcc, bcc, hcp [7] and diamond cubic materials and has been shown to

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reproduce quite well the mechanical and thermodynamic properties of the diamond α , β and liquid phases of Sn [8]. Using these potentials we calculated the diffusion activation energies of Sn in Cu and Cu in Sn and made some modifications to the previously published parameters to obtain better agreement with experiment. We will discuss these changes and will present our results on the structure and dynamics of the Sn overlayer with temperature and the correlations between Cu and Sn atoms at the interface.

METHODOLOGY AND POTENTIALS

We utilized slabs of 1800-2000 Cu atoms with 1 and 2 ML of Sn periodic in the plane of the surface (XY). The Z-direction is defined as normal to the interface. The Cu side of the slab consisted of 9 layers of which the bottom 3 were kept rigid in order to simulate a semi-infinite slab. The starting configurations were created by placing 3 layers of Sn in a simple cubic crystal geometry onto the (111) and (100) Cu slabs. These configurations were then annealed at 400 K for 10 ps in order to obtain equilibrium densities at the interface. From these relaxed slabs, the 1 and 2 ML Sn samples were obtained by removing 2 and 1 layers respectively from the annealed configurations. The resulting slabs were annealed further at 400 and 500 K for 5 ps. These slabs were then equilibrated at various temperatures in the range 300-1300 K. We monitored the dynamics and structure of the interface by looking at the radial distribution function (RDF), mean squared displacement, velocity-velocity autocorrelation function and trajectories of those atoms in the interface region over 5-10 ps time scales. The melting temperature of MEAM Cu was estimated by simulating the solid-liquid coexisting phase within a MD formalism [9]. The melting point was found to be between 1200-1400 K, thus in what follows we will use $T_m = 1300$ K and express our temperatures as fractions of the substrate melting temperature in order to more readily compare with experimental observations of Sn on other substrates [2].

The Sn-Sn, Cu-Sn and Sn-Sn interactions are described by MEAM potentials. The Cu-Sn MEAM model and fitting procedure have been reported in Ref. 10 and will not be repeated here. The Sn-Sn interaction parameters were chosen from Ref. 8, while the Cu-Cu and Cu-Sn parameters were those published in Ref. 10. Angular screening was implemented using the method detailed in Ref. 11 with $C_{min} = 0.8$, $C_{max} = 2.8$ for Sn-Sn, $C_{min} = 2.0$, $C_{max} = 2.8$ for Cu-Cu. For the Cu-Sn interactions we modified the parameter C_{min} which controls angular screening in MEAM from those used in Ref. 10 in order to optimize the migration energy of Sn in Cu and Cu in Sn since those quantities are crucial to alloy formation. The activation energy calculation of Sn in Cu was carried out employing the 5 frequency method [16] with quasi-static MD. The diffusion activation energies of Cu atoms in a Sn matrix were calculated by placing a Cu atom in various interstitial sites and displacing it with quasi-static MD to adjacent interstitial sites. The path of the Cu atoms in the direction perpendicular to the c-axis, follow a random-walk motion consisted with what is found experimentally [17]. We found that the diffusion in the parallel direction to the c-axis (β -Sn structure) is much lower than the diffusion in the perpendicular direction for the range of C_{min} values studied. This is also consisted with experimental results [17]. From these studies we selected a value of 0.8 for C_{min} in the Cu-Sn interactions. Results of these calculations are presented in Table I. Agreement with experimental values is fairly good with the notable exception of the vacancy formation energy of Sn and the activation energy of diffusion for Cu in Sn in the direction perpendicular to the c-axis. Both values are overestimated.

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PROPERTY	Theory	Experiment
$E_{1V}^f(\text{Cu})$	1.17	1.18 (a)
$E_{1V}^m(\text{Cu})$	1.08	0.71 (a)
$E_{1V}^f(\text{Sn})$	0.88	0.51 (b)
$E_{1V}^m(\text{Sn})$	0.30	0.35 (c)
$Q_{\text{Cu} \rightarrow \text{Sn}}(\text{in plane})$	1.10 (0.62)	0.34 (d)
$Q_{\text{Cu} \rightarrow \text{Sn}}(\text{in c-direction})$	0.11 (0.17)	0.17 (d)
$Q_{\text{Sn} \rightarrow \text{Cu}}$	2.03 (2.03)	1.95 (e)

TABLE I. Comparison of diffusion activation energies in Cu and Sn. All energies are in eV. Relaxed vacancy formation energy (E_{1V}^f), vacancy migration energy E_{1V}^m , activation energy of interstitial impurity diffusion of Cu in Sn ($Q_{\text{Cu} \rightarrow \text{Sn}}$) and of Sn in Cu ($Q_{\text{Sn} \rightarrow \text{Cu}}$). Values in parentheses for $C_{\min} = 0.8$, others are for $C_{\min} = 2.0$. The diffusion of Sn in Cu is through a vacancy mechanism while that of Cu in Sn is through an interstitial mechanism. The in-plane direction is perpendicular to the c-axis of the β -tin structure. (a) Ref. 12, (b) Ref. 13, (c) Ref. 14, (d) Ref. (3), (e) Ref. 15.

RESULTS

We carried out simulations with 1 and 2 ML on Sn on Cu(111) and C(100) over a temperature range 300-1300K. Our results can be summarized as follows:

- 1) No melting of the Sn overlayer was observed at any of the sampled temperatures.
- 2) On both surfaces (111) and (100), Sn seems to form a very stable, ordered structure.
- 3) No Cu-rich phases are observed and most of the Sn remains on the surface.
- 4) No significant diffusion of Sn into the substrate is observed below temperatures of $0.7 T_m$
- 5) Diffusion of Cu into the Sn overlayer is observed at lower temperatures for the Cu(111) than the Cu(100) surfaces.
- 6) The structure of the Sn interfacial layer was found to be the same for both 1 and 2 ML coverages.

Figure 1 shows the planar 2-dimensional radial distribution function (RDF) of the Sn overlayer in contact with the substrate at $0.85 T_m$, together with the RDF of the outermost Cu layer (at the interface) for both Sn/Cu(111) and Sn/Cu(100) with 1 ML coverage. The RDF curves are obtained by averaging over 5ps. From the RDFs, the structure of the Sn layer on both substrates is almost identical. The first, second and third neighbor distance between Sn-Sn atoms is approximately 3.2, 6.4 and 9.6 Å respectively on both surfaces which represents distances in the ratio 1:2:3. The sharpness of the peaks indicates that the structure remains very ordered at high temperatures. Very little difference was seen for the interfacial layer between 1 and 2 ML coverages.

FIG. 1. Two-dimensional (2D) radial distribution function (RDF) of Sn overlayer and first outermost Cu layer at $0.85 T_m$ (a) Sn/Cu(100) 1ML coverage. (b) Sn/Cu(111) 1ML coverage. The plotted RDF represent averages over 5ps. The Sn exhibits 3 sharp peaks while the Cu shows peaks corresponding to the appropriate initial structure.

At temperatures below $0.75 T_m$ the structure of the Sn overlayer on both Cu(111) and Cu(100) is squared with 4-fold symmetry. Figure 2 show a comparison between RDF of Sn on Cu(100) (1ML coverage) at two temperatures: $0.70 T_m$ and $0.85 T_m$. The 4-fold symmetry of the lower temperature phase can clearly be seen from the RDF.

FIG 2. Comparison of the in-plane (2D) RDF of the Sn-Sn atoms on Cu(100) (1 ML) at two different temperatures. The structure at 900 K ($0.70 T_m$) is a distorted square structure with distances in the ratio: 1:1.414:2:2.44, while the one at 1100 K ($0.85 T_m$) has distances in the ratio 1:2:3. The RDF at 900 K has been displaced vertically for clarity.

More detail of the structure of the overlayer at $0.85 T_m$ is provided by the atomic trajectories. In Figure 3 we show the motion of the atoms on the surface layer over a 5 ps time period. The structure appears to contain regions of squares and hexagons. It is interesting to see that such a complex structure leads to the simple RDFs shown in Figure 1. We are currently looking more carefully at these structures. The atoms trajectories clearly show that the motion is more vibrational than diffusional. The root mean squared (RMS) motion of the Sn atoms on the overlayer is about the same as the Cu atoms in the outermost bilayer. Diffusive motion in the Z-direction is not

FIG. 3. Top view (XY) of the trajectories of 1 ML of Sn atoms on the (111) (a) and (100) (b) surfaces of Cu at $0.85 T_m$. The circles in (a) indicate Cu atoms. Regions of 4-fold and 6-fold symmetry are seen.

observed until temperatures above $0.75 T_m$. This temperature is much higher than recent experiment results which indicate that a stable alloy phase does not form on Cu(111) for annealing temperatures below $0.42 T_m$ [2]. In Figure 4 we show the temperature dependence of the diffusion of the Sn atoms in the direction perpendicular to the surface (Z-direction). No surface evaporation is taking place at these temperatures (700-1300 K), thus this indicates the Sn atoms are mostly diffusing into the substrate.

Although, it has not been presented here, modification of the screening parameters of Cu-Cu potentials which result in a lower melting point show alloy formation at much lower temperatures. This might indicate that the vibrations at the surface (RMS motion) might place a crucial role in the diffusion and alloy formation at the Cu-Sn interface

FIG. 4. Diffusion of Sn atoms in the direction perpendicular to the surface (Z-direction). The activation energy estimated from the slope at high temperatures is $Q=0.44$ eV.

CONCLUSIONS

We have calculated the activation energies of diffusion of Cu in Sn and Sn in Cu (dilute cases) employing a MEAM interaction model of the Cu-Sn system. We find fairly good agreement with experimental values with the notable exception of the diffusion of Cu in Sn in the direction perpendicular to the c-axis where we predict a value almost twice as large as the experimental value. We carried out Molecular Dynamics simulations of thin Sn overlayers (1-2 ML thick) on the (111) and (100) surfaces of Cu over a wide temperature range (300-1300 K). We find the Sn forms a very stable incommensurate structure which appears to be the same for both surfaces. This structure remains ordered at high temperatures (1100-1300 K). We find no significant diffusion of Cu into the Sn overlayer or Sn into the substrate at temperatures below $0.70 T_m$.

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