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Abstract
The melting behaviour of Pb film embedded in an Al matrix has been
investigated by a molecular dynamics simulation technique. The Sutton–Chen
potential for alloys has been employed to perform these calculations. Melting
of a Pb(110) film has been studied by embedding it in Al(110) and Al(111).
Melting is found to initiate at the film–host interface for the Al(110) host.
However, a change in orientation of the film is observed before superheating
when the film is embedded in the Al(111) matrix. The superheating determined
by simulation is comparable with the value calculated by homogeneous theory.

1. Introduction

The melting of solids has been a subject of many theoretical and experimental investigations for
a long time to establish the mechanism by which it is initiated. The possible role of the surfaces
in nucleating melting has commonly been argued. The melting behaviour of different surface
orientations of a metal has been reported to be contrasting in many f.c.c metals [1–3]. Both
experiments and molecular dynamics simulation show that the more open crystal surfaces like
Pd(110) [3], Pb(110) [4] and Al(110) [5, 6] premelt at a temperature much lower than the bulk
melting temperature. In contrast to this, Herman and Elsayed-Ali [2] have found superheating
of Pb(111) up to 120 K above bulk melting temperature. This superheating was studied by time
resolved reflection high energy electron diffraction and it involved bypassing the effect of the
free surface by rapid heating of about 10^{11} K s^{-1} with a pulsed laser beam. Many studies have
demonstrated that encapsulating crystallites within higher melting-point host matrices may give
rise to superheating as well [7–14]. For example the melting temperature of silver clusters
have been elevated up to 25 K above the silver melting point by gold coating [7]. Superheating
has been reported, by x-ray diffraction, in lead precipitates embedded in an Al matrix [15, 16].
These studies have shown that surface melting depends upon the degree of surface packing,
with open surfaces demonstrating surface melting. Superheating of 200 K has also been

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reported in the compressed Pb epitaxy on Cu(111) substrate [17], whereas a Pb monolayer, grown on the more open Cu(110) substrate, was shown to undergo an order–disorder transition at lower temperature [18, 19]. However, the role of host matrix orientation has not been given much consideration in the case of melting of embedded films. In the present study we apply the molecular dynamics simulation technique to investigate the melting of Pb(110) crystals embedded in two different orientations of Al matrix to demonstrate the significance of matrix orientation. In the first case we confined a Pb(110) film in the Al(110) matrix and in the second case a Pb(110) film was confined in the Al(111) matrix.

2. Computational technique

We have employed the Sutton–Chen many body glue potentials [20] for Al and Pb in these studies. The potential has been modified for Al–Pb alloys [21, 22] and has already been applied successfully to understand the melting of Pb clusters embedded in an Al matrix [22]. Simulation was carried out under the conditions of constant pressure (NPT). The initial configurations were generated by using the lattice parameters of Al and Pb, calculated from separate NPT simulations for these metals. The MD cell for the Al(110)/Pb(110) system was constructed from 24 (110) planes of Al, with 220 atoms in each layer and ten (110) layers of Pb, with 144 atoms per layer. The number of layers for Pb (110) was chosen so that the stacking sequence of the host Al remained unchanged with the introduction of Pb film. The film was located symmetrically between the Al matrix. The model consisted of 6720 atoms. For the Al(111)/Pb(110) system the model consisted of 6180 atoms with 24(111) layers of Al and 10(110) layers of Pb. A Pb(110) film, with 90 atoms in each layer, was generated in the middle of an Al matrix with the Al–Pb interlayer distance set close to the average of the interlayer distances of Al and Pb. Periodic boundary conditions were applied in all three directions. A Verlet algorithm with a time step of 5×10^{-15} s was used to solve the equations of motion. The system was equilibrated at 100 K for 8000 time steps before heating up to 800 K at a rate of 5×10^{12} K s^{-1}. In the second case the system was heated up to 1000 K at the same heating rate.

3. Results and discussion

The simulation was started with the situation where a Pb(110) film was embedded in the similar structure of an Al matrix i.e., Al(110). The average energy per atom as a function of temperature for the Pb(110) film as well as the host Al(110) is shown in figure 1. The energy varies linearly with temperature for Al over the whole range of temperature. For the Pb(110) film the change is linear up to 580 K and then there is an upward rise in the slope. The melting point of the film is estimated to lie between 580 K and 600 K, which is close to the melting temperature of surface-free Pb(110). The atomic configurations of the film and the host at selected temperatures have been recorded and plotted in figure 2. The plot of atomic positions at 100 K shows that there exist two semi-coherent interfaces between the film and the host. The structure remains crystalline at 550 K. The film is in a molten state at 600 K, thus suggesting that melting has taken place at a temperature between 550 K and 600 K. Melting is found to initiate heterogeneously at the matrix–film interface. The thin disordered layer formed at the interface acts as a nucleus for melting the film, thus precluding superheating.

The melting behaviour of Pb(110) film is also examined after confining it in the close packed host of Al(111). The average energy per atom was recorded as a function of temperature and is given in figure 3. The energy of the film increases linearly with temperature up to about
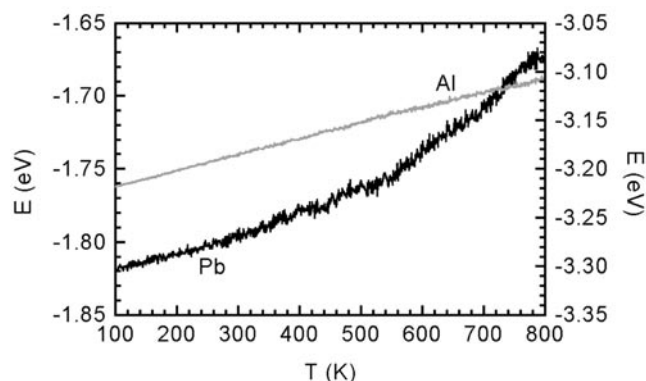
Figure 1. Variation of potential energy per atom with temperature for the Pb(110)/Al(110) system.
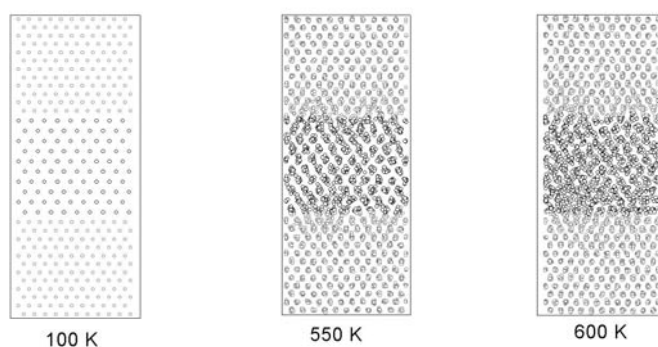

Figure 2. Snapshots of atomic positions at selected temperatures for the Pb(110)/Al(111) system. The structure is projected on to the x–z plane. The film lies in the middle.

530 K and then there is an upward increase in slope. It reaches to a maximum value at about 590 K and then drops again. It remains constant up to 720 K and then rises again. There is a sharp transition in the energy at about 900 K. The energy of the host i.e. Al increases in a linear manner with temperature and only a slight kink is observed at the temperature where a peak is observed in the Pb energy. The atomic positions were recorded at various temperatures to examine the variations taking place in the structure. In the starting configuration, i.e. at 0 K, two incoherent interfaces are present between the host and the film. The film remains perfect (110) up to 530 K and a plot at 300 K is given in figure 4 to show the structure in this condition. Nucleation is found to take place in the film and the structure is distorted at 550 K as can be seen from the atomic positions at this temperature. The structure undergoes a change of orientation from (110) to (111) at 600 K and ten (110) layers are transformed to six (111) distorted layers (figure 4). The structure of the film becomes perfect (111) at 650 K with lower energy and six layers can be seen clearly from figure 4. Melting initiates, again inside the film, at about 900 K as shown in a plot of coordinates in this condition.

Another parameter, which can show the ordering of the structure, is the number density of atoms along the perpendicular direction, i.e. the z-direction in our case. The number density has been calculated at different temperatures to understand the changes taking place at these temperatures. These results are plotted in figure 5. The sharp peaks at 300 K represent ten well defined layers of the Pb(110) film. The peaks become broader as the temperature rises
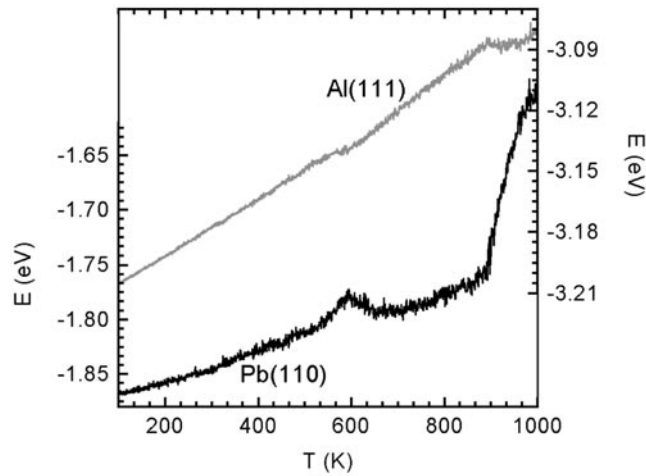
Figure 3. Variation of potential energy per atom with temperature for the Pb(110)/Al(111) system.
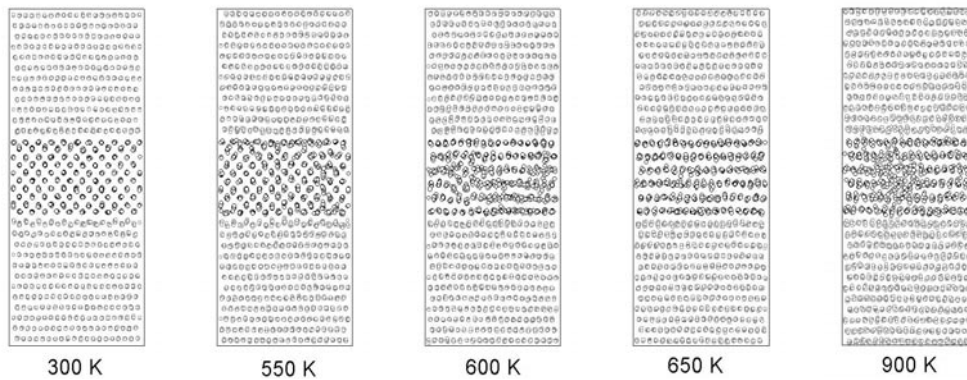

Figure 4. Snapshots of atomic positions at selected temperatures for the Pb(110)/Al(111) system. The structure is projected on to the x–z plane. The film lies in the middle.

as shown in a plot at 550 K. The spread in the peaks at 550 K clearly shows the disorder in the structure. Apart from the two outermost layers all the layers are destroyed. The plot at 600 K shows six peaks instead of ten original peaks. This indicates a structural change from ten layers to six layers in the film and the broadening of the peaks suggests the disorder present at this temperature. The structure becomes well ordered at 650 K (figure 5) with a sequence corresponding to (111) structure. Melting initiates inside the film as can be seen from the plot at 900 K, where outermost layers are still well defined and the inner layers are almost destroyed.

The results indicate that for the open Al(110) host, melting initiates at the film–host interface at a temperature where free surface Pb(110) melts. No superheating is observed in the Pb(110)/Al(110) system even for such a high heating rate. This finding is in agreement with the experimental observations [2, 23] where laser heating of the system has been performed and no superheating was observed for Pb(110). In case of Pb(110)/Al(111), homogeneous nucleation takes place within the film at a temperature close to melting temperature of the free Pb(110) surface. It is interesting to note that confinement in the close packed structure
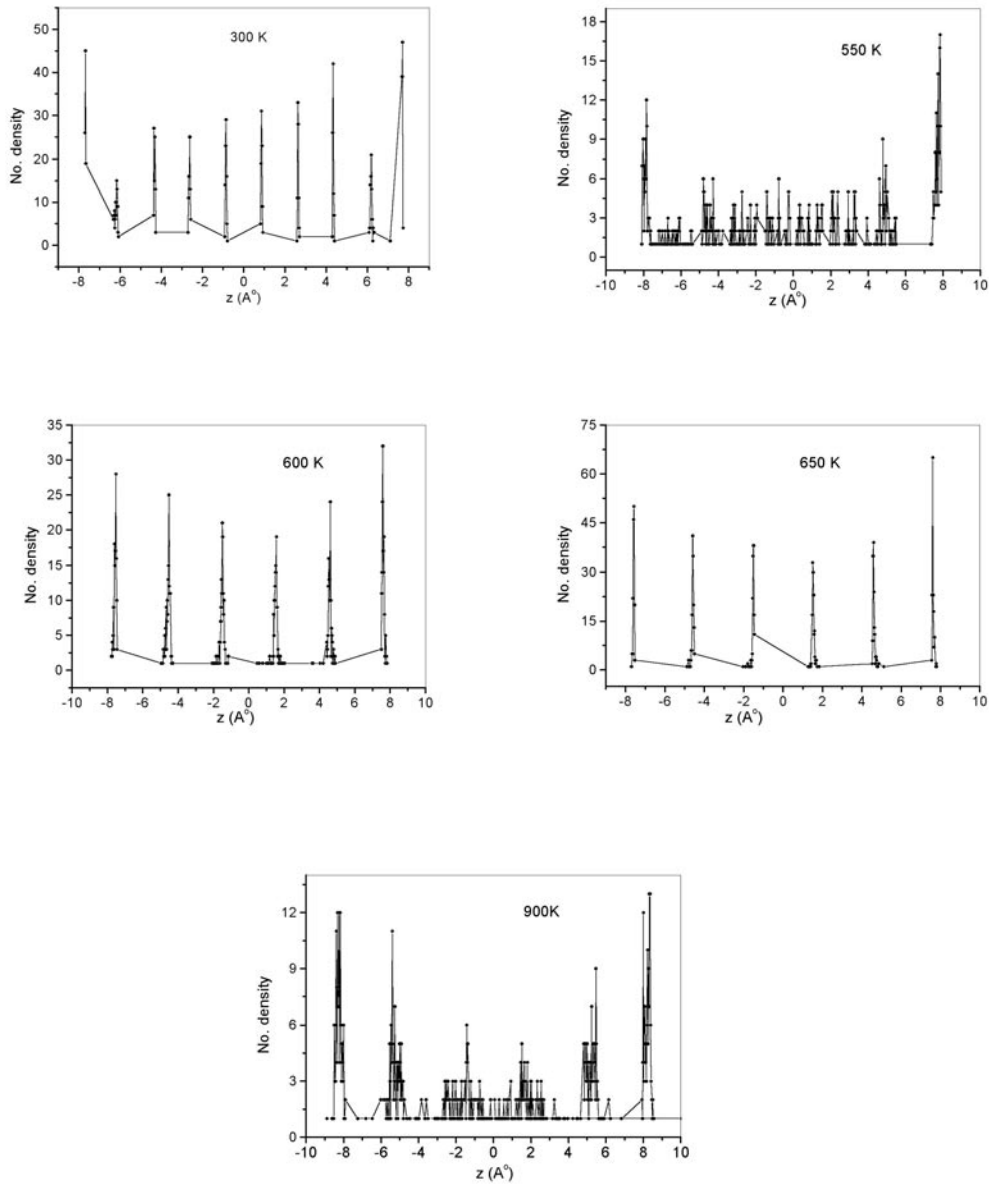
Figure 5. Atomic density profiles along the z direction at selected temperatures for the Pb(110)/Al(111) system.

of the matrix change the film orientation from open Pb(110) to the close packed Pb(111) at a temperature close to the bulk melting temperature. This change in structure takes place due to the reduction in interfacial energy. This change of orientation near melting temperature is in agreement with the experimental findings of Peters *et al* [24], where it has been shown, by x-ray studies, that the crystallites rotate and reorient themselves to a low energy Pb(111) structure near melting. Such preferred host–film relative orientation has also been predicted by Novaco and McTague [25] for the growth of adbsorbate on dissimilar substrates.

The results are analysed on the basis of the classical homogeneous nucleation theory [26], according to which, for a pure substance, the Gibbs free-energy difference between a crystalline and a liquid embryo of spherical shape of radius r can be written as

$$\Delta G = \tfrac{4}{3}\pi r^3(-L_0 \Delta T/T_0 + \Delta E) + 4\pi r^2 \gamma_{sl} \tag{1}$$

where T_0 is the thermal equilibrium melting temperature, L_0 is the latent heat at T_0, γ_{ls} is the solid–liquid interfacial free energy, ΔT is the degree of superheating and ΔE represents the strain effects caused by volume change on melting [5]. From $\partial(\Delta G)/\partial r = 0$, a relationship between the critical radius r_c and ΔT obtained is

$$\Delta T/T_0 = (2\gamma_{sl}/r_c + \Delta E)/L_0. \tag{2}$$

For a thin-film of thickness d sandwiched between semi-infinite solid matrices, a similar relation can be written:

$$\Delta T/T_0 = [2(\gamma_{lm} - \gamma_{sm})/d + \Delta E']/L_0 \tag{3}$$

where $\gamma_{lm} - \gamma_{sm} = \gamma_{ls}$ is the difference between liquid–matrix and solid–matrix interfacial energy, and $\Delta E'$ denotes the strain effects caused by volume expansion as well as by the thermal expansion mismatch on melting. Using the data for Pb from the literature, $\gamma_{ls} = 0.097$ J m^{-2} [24], $L_0 = 4.81$ kJ mol^{-1} [27] and $\Delta E = 0.1L_0$, and $d = 17.2$ Å (the thickness of our film) we calculated, $\Delta T/T_0 = 0.53$ or $\Delta T = 0.53T_0$. This value compares very well with our simulated value of $0.50T_0$. However, the superheating is much higher than 120 K, obtained experimentally by Herman and Elsayed-Ali for Pb(111) [2]. A possible reason for this higher value may be the fact that 900 atoms of ten Pb(110) layers are packed into six Pb(111) layers and this increases the density of Pb(111) planes by 4.17% more than the normal density. Furthermore, the heating rate in our simulation is higher than the one used by Herman and Elsayed-Ali in their experiment [2]. This increase in melting temperature due to increase in density is in agreement with the experimental findings of Meyer *et al* [17], where a rise of 200 K in melting temperature has been reported, by LEED studies, in a 3.2% compressed layer of Pb epitaxy on Cu(111).

4. Conclusions

In conclusion we have shown that the superheating of a confined film is influenced by the orientation of the host matrix. Pb(110) can never be superheated by embedding into the Al(110) host. However, Pb(110) film shows orientation transition from (110) to (111) when confined in Al(111) host. The reoriented structure is superheated up to 300 K above the bulk melting temperature and this value in agreement with the theoretical calculated value. Therefore the results reported here signify the importance of the matrix orientation in which the film is confined.

Acknowledgments

References

[1] Pluis B, Denier van der Gon A W, Frenken J W M and van der Veen J F 1987 *Phys. Rev. Lett.* **59** 2678

  [2] Herman J W and Elsayed-Ali H E 1992 *Phys. Rev. Lett.* **69** 1228
  [3] Akhter J I, Yaldram K and Ahmad W 1996 *Solid State Commun.* **98** 1043
  [4] Allen G L, Gile W W and Jesser W A 1986 *Thin Solid Films* **144** 297
  [5] Allen G L, Gile W W and Jesser W A 1985 *Acta Metall.* **28** 1695
  [6] Rossouw C J and Donnelly S E 1985 *Phys. Rev. Lett.* **55** 2960
  [7] Dages J, Gleiter H and Perepezko J H 1986 *Phys. Lett.* A **119** 79
  [8] Saka H, Nishikawa Y and Imura T 1988 *Phil. Mag.* A **57** 895
  [9] Goswami R and Chattopadhyay K 1993 *Phil. Mag. Lett.* **68** 215
 [10] Zhang D L and Cantor B 1990 *Phil. Mag.* A **62** 557
 [11] Zhang D I and Cantor B 1991 *Acta Metall. Mater.* **39** 1591
 [12] Malhotra A K and Van Aken D C 1995 *Phil. Mag.* A **71** 949
 [13] Sheng H W, Ren G, Peng L M, Hu Z Q and Lu K 1996 *Phil. Mag. Lett.* **73** 179
 [14] Chattopadhyay K and Goswami R 1997 *Prog. Mater. Sci.* **42** 287
 [15] Grabaek L, Bohr J, Johnson E, Johansen A, Sarholt-Kristensen L and Andersen H H 1990 *Phys. Rev. Lett.* **64** 934
 [16] Grabaek L, Bohr J, Johnson E, Johansen A, Sarholt-Kristensen L and Andersen H H 1992 *Phys. Rev.* B **45** 2628
 [17] Meyer G, Michailov M and Henzler M 1988 *Surf. Sci.* **202** 125
 [18] Georgiev N and Michailov M 1988 *Phys. Rev.* B **58** 13 895
 [19] Michailov M, Beauvais de C Rouxel D and Mulaftschiev B 2000 *Phys. Rev.* B **61** 5987
 [20] Sutton A P and Chen J 1990 *Phil. Mag. Lett.* **61** 139
 [21] Rafii-Tabar H and Sutton A P 1991 *Phil. Mag. Lett.* **63** 217
 [22] Jin Z H, Sheng H W and Lu K 1999 *Phys. Rev.* B **60** 141
 [23] Herman J W and Elsayed-Ali H E 1992 *Phys. Rev. Lett.* **68** 2952
 [24] Peters K F, Cohn J B and Chung Y W 1998 *Phys. Rev.* B **57** 13 430
 [25] Novaco A D and McTague J P 1977 *Phys. Rev. Lett.* **38** 1286
 [26] Uhlamann D R 1980 *J. Non-Cryst. Solids* **41** 347
 [27] Porter D A and Easterling K E 1980 *Phase Transformations in Metals and Alloys* (London: Van Nostrand Reinhold) p 171