Molecular dynamics study of the mechanical characteristics of Ni/Cu bilayer using nanoindentation

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In the present work, a three-dimensional molecular dynamics simulation is carried out to perform the nanoindentation experiment on Ni single crystal. The substrate indenter system is modeled using hybrid interatomic potentials including the many-body potential embedded atom method (EAM), and two-body morse potential. To simulate the indentation process, a spherical indenter (diameter = 80 Å, 1 Å=0.1 nm) is chosen. The results show that the mechanical behaviour of a monolithic Ni is not affected by crystalline orientation. To elucidate the effect of a heterogeneous interface, three bilayer interface systems are constructed, namely Ni(100)/Cu(111), Ni(110)/Cu(111), and Ni(111)/Cu(111). The simulations along these systems clearly describe that mechanical behaviour directly depends on the lattice mismatch. The interface with the smaller mismatch between the specified crystal planes is proved to be harder and *vice versa*. To describe the relationship between film thickness and interface effect, we choose various values of film thickness ranging from 20 Å to 50 Å to perform the nanoindentation experiment. It is observed that the interface is significant only for the relatively small thickness of film and the separation between interface and the indenter tip. It is shown that with the increase in film thickness, the mechanical behaviour of the film shifts more toward that of monolithic material.

Keywords: nanoindentation, bilayer, molecular dynamics, thin film

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1. Introduction

Multilayered metallic films have attracted much attention in the last few years due to their diverse mechanical behaviours on the nanometer scale as compared with bulk materials.[1−3] Multilayered thin films have potential applications in many areas, such as microelectromechanical systems, protective coatings, magnetic media, high-density storage systems, etc.[4−6] The mechanical behaviour of multilayered film is of great interest particularly because of the increase in the elastic modulus, and the yield strength of the material has been predicted previously by many researchers.[7] Therefore, it is necessary to elucidate the mechanical behaviour of multilayered film to improve the reliability of thin film products on the nanoscale.[8] Among many methods utilized in nanotechnology, the nanoindentation versatile mechanical technique is most widely used for inspecting the mechanical behaviours of multilayered metal films such as elastic constant and hardness.[9−11] Recently, it has become a very popular technique for investigating mechanical characteristics of metal thin films.

The basic principle of the nanoindentation process is very simple, i.e., an indenter with predefined shape and size is set to move into the substrate and the resulting applied load and indenter depth are measured. These are raw output results of the nanoindentation experiment and can be further used to characterize the sample substrate through post analysis.[12,13] Immense theoretical and experimental work has already been reported to characterize the nanoindentation process including the adhesion of the sample atom with the indenter tip, substrate fracture,[14,15] elastic-plastic contact behaviour,[16] and phase transformation during indentation loading.[17] A series of nanoindentation experiments has been reported to understand the fracture toughness model of brittle film on the ductile substrate using the indentation technique.[18] Nanoindentation was simulated to understand the effect of twin boundaries parallel to the indented surface of (111) film. Twin boundary appearing as an effective obstacle to the dislocation propagation dominates the defor-

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mation process, resulting in film hardening.[19] Deformation induced grain growth in Ni film was reported during a nanoindentation experiment and was found to be thermally activated.[20] Hardness measurement was found to be significantly dependent on the indentation size and substrate for hard and soft films.[21]

Molecular dynamics (MD) simulation, a well-known method, has previously been widely used to simulate nanoindentation problems.[22] The MD simulation was performed to study nanoindentation induced plastic deformation in a copper (Cu)/nickel (Ni) system. It was reported that Cu films interestingly show significant strengthening by the thin Ni coating especially at low temperatures.[23] Nanoindentation of bilayer aluminum (Al) thin film deposited on a silicon (Si) substrate was simulated using MD to show significant hardness dependence of loading rate, and the substrate dependence of pile-up behaviour of the metallic film was also investigated.[22] Nanoindentation was used to describe the mechanical behaviours of metallic thin films deposited on different substrates. Determination of true hardness made it possible to examine the effect of elastic constant mismatch on the mechanical characteristics of the film substrate system.[24] MD simulation of Cu was performed to investigate the effect of crystallographic orientation on the crystalline plasticity.[25] During MD investigation the most common mechanism of dislocation misfit accommodation was the emergence of misfit through the film substrate interface.[26] The Cu/Ni system showed a significant so-called super modulus effect which is enhanced at bilayer thickness of about 2 nm. Results of the Vickers hardness test on a multilayered Cu/Ni system also show hardness enhancement similar to the consequence of super modulus effect.[27–29] Synthesis of mechanical properties highly texturing multilayered (111) and (100) Cu/Ni films was carried out for film thickness values ranging from 1 nm–200 nm.[30]

Despite the above mentioned studies, immense work is still required for completely understanding the mechanism relating to nanoindentation of multilayered thin film. In the present work, our attention is paid to the MD simulation of a Cu/Ni bilayer system and some effects of layer orientation are analysed. Firstly, nanoindentations of monolithic Ni are performed along different crystalline orientations and their effects are observed. Secondly, the effects of different orientations of Ni film with constant film thickness on a Cu substrate are explained. Moreover, the effects of orientation mismatch at Cu and Ni interfaces are investigated and maximum load and hardness for the indentation process are measured. Finally, Ni films of various thicknesses are deposited on the Cu substrates and nanoindentation characteristics are investigated.

2. Sample preparation

The configuration of a typical simulated indenter and film/substrate system is shown in Fig. 1. The film material is Ni having face centred cubic (fcc) lattice with a lattice constant of 3.52 Å, and the substrate is of Cu having a lattice constant of 3.62 Å. The typical film/substrate sizes are 150 Å × 150 Å ×100 Å along (1 1 −2), (1 −1 0), and (1 1 1) directions respectively. A spherical diamond indenter (diameter = 80 Å) with (100) tip toward the substrate is used for investigating the indentation process. Firstly, monolithic Ni(100), (110), and (111) are simulated for the indentation process. Secondly the Ni films of thickness 20 Å and orientations (100), (-110), and (111) respectively are deposited on the Cu(111) surfaces to investigate the mechanical characteristics of the film/substrate system. Single crystal Ni(100), (-110), and (111) substrates of the same dimensions are also individually indented so that results may be compared with those of the film/substrate systems. Finally, the Ni films with various thickness values (20 Å, 30 Å, 40 Å, and 50 Å respectively) are deposited on the Cu substrates to investigate the effect of film thickness on the mechanical behaviour.

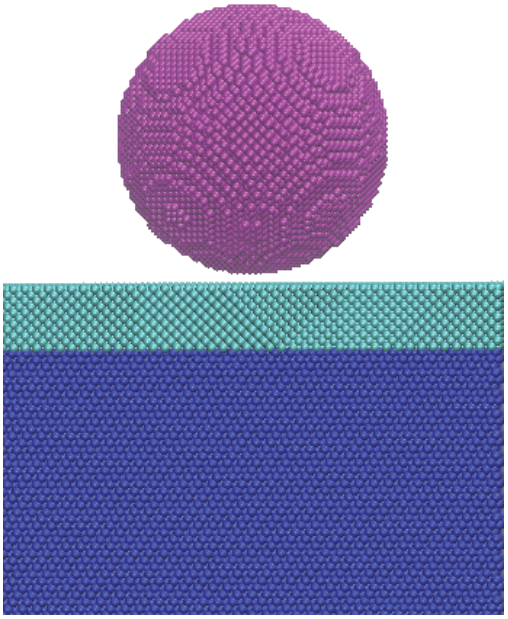


Fig. 1. (colour online) A typical simulation cell having a Ni/Cu bilayer with diamond indenter.

3. Interatomic potential

In the present work, the computational cell consists of three types of atoms, i.e., Cu, Ni, and diamond (C). There are several types of interactions that possibly take place in the simulation process as explained below.

(i) The interactions of Ni–Ni, Ni–Cu, and Cu–Cu atoms are described by the well-known embedded atom method (EAM) potential[31,32] where the total energy $E_{\rm tot}$ of this potential model can be calculated as

$$E_{\rm tot} = \sum F_i(\rho_{{\rm h}i}) + \frac{1}{2}\sum_i \sum_{j(\neq i)} \phi_{ij}(R_{ij}).$$

In this expression $\rho_{{\rm h},i}$ is the electron density of the host atom i, $F_i\,(\rho_{{\rm h},i})$ is the energy of the embedded atom into the background electron density ρ, and $\phi_{ij}\,(R_{ij})$ is the core–core pair repulsion between the atoms i and j separated through a distance R_{ij}.

(ii) Two-body Morse potential is used to describe the interactions of C–Ni and C–Cu atoms which are extensively used in MD simulation.[22] The Morse potential energy, $U_{\rm Morse}(r_{ij})$, can be described with three parameters as

$$U_{\rm Morse}(r_{ij}) = D[\,{\rm e}^{2-\alpha(r_{ij}-r_0)} - 2\,{\rm e}^{-\alpha(r_{ij}-r_0)}],$$
$$r_{ij} < r_c,$$

where D is the cohesion energy of exchange interaction, r_0 is the equilibrium distance, r_{ij} is the separation distance between atoms i and j, and α is fitted to the bulk modulus of the material. For C–Ni atoms the Morse potential parameters D, α, and r_0 are 1.0094 eV, 1.9875 Å^{-1}, and 2.56 Å, respectively and for C–Cu atoms, the values of D, α, and r_0 are 0.087 eV, 1.7 Å^{-1}, and 2.2 Å, respectively.[33]

(iii) C–C atoms of the indenter are all taken as rigid and treated as a single particle hence no description is required for the interaction.

4. Simulation process

In the present work nanoindentation is simulated using the MD simulation technique. The large-scale atomic/molecular massively parallel simulator (LAMMPS)[34] package is used to perform the simulation throughout this work. The bottom three layers of the substrate Cu are kept unchanged, periodic boundary conditions are applied along the sides of the substrate whereas the upper part is subjected to free boundary conditions. The diamond indenter sphere is treated as being rigid and is placed 3 Å above the top surface of the substrate. The force acting on an individual particle of an indenter is calculated by summing the force contributions of the surrounding atoms. The substrate is first relaxed to minimum energy using the conjugate gradient method. Equilibration is performed using Nose–Hover scheme and temperature of the system is kept constant (300 K) using the velocity rescaling method. A time step of 1 fs is chosen for time integration of Newton's equation of motion. The projected contact area is calculated using formula

$$A = \pi R d,$$

where R and d are the radius of indenter sphere and indentation depth respectively. Hardness is calculated using the following relation:

$$H = \frac{F_{\rm max}}{A_c},$$

where $F_{\rm max}$ and A_c are the maximum indentation load and projected contact area respectively.

5. Results and discussion

5.1. Nanoindentations of single crystal Ni along different crystallographic orientations

A spherical indenter is subjected to moving with a constant velocity of 100 m/s to indent the substrate of each crystallographic orientation to investigate the effect of crystal orientation on the mechanical behaviour of the pure Ni. In order to characterize the indentation process, load is calculated by measuring the average force experienced by atoms of the indenter. The load–depth curves for each orientation are plotted as shown in Fig. 2. It can be observed that curves

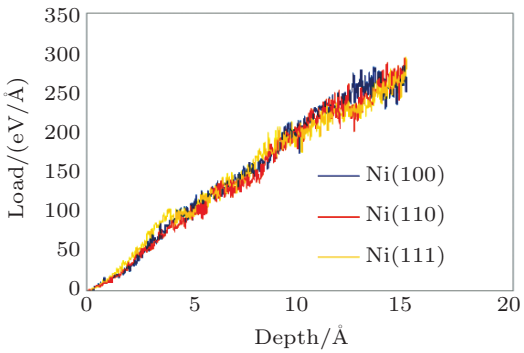


Fig. 2. (colour online) Load versus depth plot to describe the effect of various crystalline orientations in monolithic Ni.

for each orientation coincide with each other, which clearly shows that load–depth curves have the same slopes, i.e., hardness values of the Ni are the same along all crystal orientations. These results can also be observed in the hardness-depth plot as shown in Fig. 3.

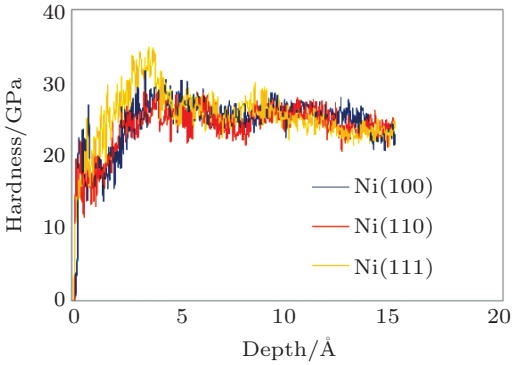


Fig. 3. (colour online) Hardness versus depth plot to describe the effect of various crystalline orientations in monolithic Ni.

It is clear from Figs. 2 and 3 that the hardness of a monolithic material is independent of the crystalline orientation. The oscillatory periods of curves are slightly different from each other, which may be due to the difference in slip direction in different indentation processes for each orientation. The behaviours of the present results are supported by the previous theoretical and experimental work.[35]

5.2. Nanoindentation of Ni/Cu (film/substrate) system

In order to investigate the effects of heterogeneous interfaces between Ni film and the Cu substrate, we choose three configurations of (film/substrate) systems as follows: i) Ni(100) film deposited on Cu(111) substrate, ii) Ni(110) film deposited on Cu(111) substrate, iii) Ni(111) film deposited on Cu(111) substrate.

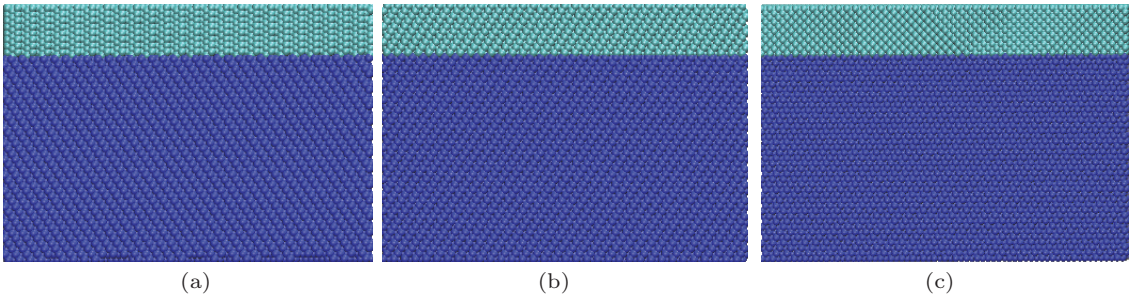


Fig. 4. (colour online) Films Ni(100) (a), Ni(110) (b), and Ni(111) (c) deposited on Cu(111), respectively.

All the samples are first allowed to fully relax to their minimum energy levels using the conjugate gradient method so that the interface atoms adjust themselves to minimize the effect of internal stresses. Thickness of Ni film is 20 Å for all orientations. Each film is indented using a spherical indenter subjected to moving with a constant velocity of 100 m/s. The indentation stops at a maximum depth of 14 Å and load is measured at each simulation step. To analyse the mechanism of indentation, resulting load VS depth curves for each crystal orientation are compared as shown in Fig. 5. We also compare the results of hardness each plotted as a function of indentation depth to more deeply analyse the underlying mechanical phenomenon in the loading process. Comparison between hardness versus depth curves is shown in Fig. 6.

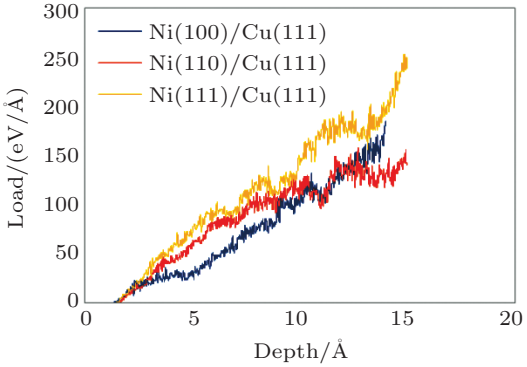


Fig. 5. (colour online) Load versus depth plot to describe the effect of heterogeneous interfaces.

Figure 5 shows the load–depth curves corresponding to the indentation processes at a velocity of 100 m/s. Blue curve represents indentation load versus depth for Ni(100)/Cu(111) system, red curve

represents load versus depth for Ni(110)/Cu(111) and yellow curve represents load–depth relationship for Ni(111)/Cu(111). It is clear that for the same depths the maximum load is higher for Ni(111)/Cu(111) than that for Ni(110)/Cu(111) system, whereas Ni(110)/Cu(111) bilayer film has a high maximum load as compared with Ni(100)/Cu(111) bilayer film. It means that the resistance to indentation process is enhanced in Ni(111)/Cu(111) as compared with that in the other two configurations.

Figure 6 presents the comparison of hardness-depth relationship among three bimetallic configurations. We can see that for particular values of depth the hardness values are also high for Ni(111)/Cu(111) as compared with that for the other two orientations of the film/substrate system, although the value of hardness is lower than that of the corresponding monolithic Ni but it is still considerably higher than that of monolithic Cu. This hardening effect is due to the presence of lattice mismatch between Ni and Cu at the interface. The initial cubic system in Ni/Cu evolves into the tetragonal system ($a = b \neq c$) at the interface, and the internal stress may also cause dislocations to be initiated from the interface in the relaxation process.[35] The difference in the hardness along different Ni/Cu orientations is suggested to be due to the mismatch of lattice spacing, i.e., the higher the mismatch, the more difficult the adjustment of the atom to a possible lower energy level is. The mismatch can be easily described by using the measured lattice parameter (lattice spacing) of each planner configuration. The lattice parameter can be measured using the MD simulator LAMMPS.[34] The percentage mismatches for all three systems are summarized as follows: Ni(100)/Cu(111) 43.782%, Ni(110)/Cu(111) 20.496%, Ni(111)/Cu(111) 2.628%.

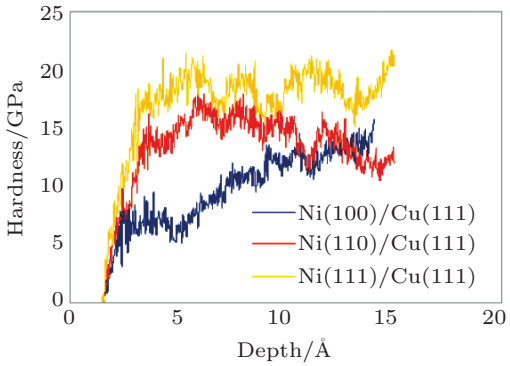


Fig. 6. (colour online) Hardness versus depth plot to describe the effect of heterogeneous interfaces.

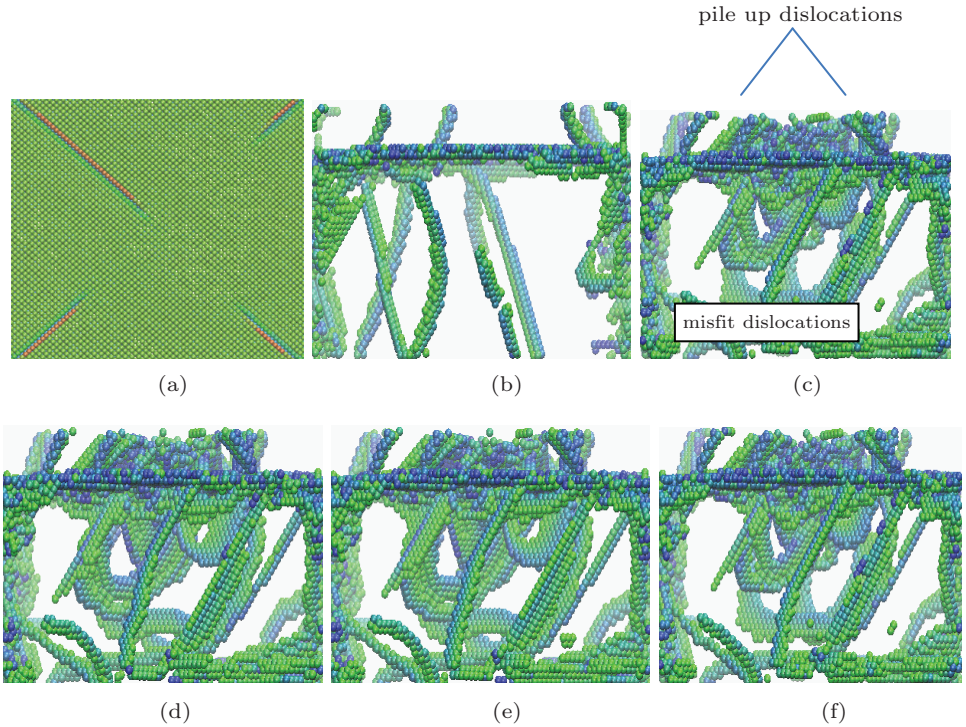


Fig. 7. (colour online) Upper view of interface induced dislocations prior to indentation (a), side view of Ni(100)/Cu(111) interface prior to indentation clearly showing initial dislocation configuration (b), and different stages of indentation induced dislocations ((c)–(d)). These panels clearly show that the interface acts as an effective obstacle to dislocation propagation and that dislocations nucleate at the interface. Atoms are colored using the CSP method.

The degree of mismatch can also be understood easily in terms of the percentage mismatch of the given system. Hence the Ni(111)/Cu(111) system with the least mismatch is hardest and *vice versa*. When the indenter penetrates the film, defects and dislocations are produced and dislocations start moving towards the interface. Initially the interface acts as an effective obstacle to the propagation of the dislocations but after the passage of the first dislocation the further dislocation movement becomes easy. This effect is also reported in Ref. [23]. The dislocations produced in the indentation process can be displayed easily using the centro symmetry parameter (CSP) and the snapshots may be created using visual molecular dynamics (VMD) software.[36] Snapshots of dislocation produced due to the presence of interface and indentation induced deformation are shown in Fig. 7.

The deformation process involves dislocation pile-ups in the interface and dislocation transmission through the Ni/Cu interface. The interface slip is also considered, for the initial position of misfit dislocations can ease the transmission of dislocation through the interface. Indentation induced deformation involves several partial dislocations, and for fcc crystal the partial dislocations move on (111) slip plane as frequently observed in the literature.[37,38] Valuable discussion about dislocation movement is available in Refs. [23], [25], and [39].

5.3. Effect of film thickness

In this part of the paper, we investigate the effect of film thickness on the mechanical behaviour of the film/substrate system. For this purpose we choose the Ni(111)/Cu(111) (film/substrate) systems with film thickness values of 20 Å, 30 Å, 40 Å, and 50 Å respectively. The substrate is first allowed to fully relax using the conjugate gradient method and a rigid spherical indenter is set to indent the film with a constant velocity of 100 m/s. Each sample is indented up to a maximum depth of 14 Å. To characterize the mechanical behaviour of the film/substrate system, the curves of load versus depth and hardness versus depth are plotted in Figs. 8 and 9, respectively.

Figures 8 and 9 present the curves of load–depth and hardness–depth corresponding to an indentation depth of 18 Å and indenter velocity of 100 m/s. The blue, orange, yellow, and green lines represent the results of film thickness values of 20 Å, 30 Å, 40 Å, and 50 Å respectively. From Fig. 8 we can see that the load–depth curves coincide well with each other up to the indentation depth of 8 Å. As the indentation depth exceeds this critical value, the load starts to descend for the 20-Å film as compared with the cases of high thickness values. A similar effect is also observed in the previously reported work.[22] However, curves for 30 Å, 40 Å, and 50 Å thick films show higher values of the loads and still coincide well with each other. This reduction in the value of load for the 20-Å film in comparison with the higher thickness is suggested to be due to the presence of the interfaces closer to the indenter tip. When the separation between the indenter tip and the interface increases the mechanical behaviour of the film tends towards the mechanical behaviour of the monolithic Ni material. This reveals that the effect of the interface is significant only for smaller thicknesses when the indenter tip and interface are closer and negligible for higher thicknesses. A similar behaviour can be observed from the hardness–depth curves presented in Fig. 9. Curves for higher thickness also show slightly descending load and hardness, which is believed to be due to the deformation and slipping of the single crystal atomic layer in the indentation process. Hence the interface is effective only

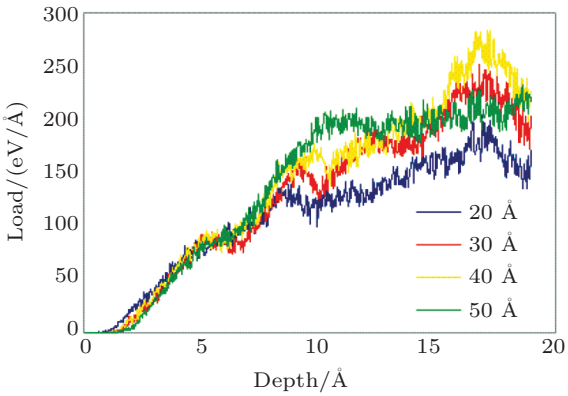


Fig. 8. (colour online) Load versus depth plot to describe the effect of film thickness.

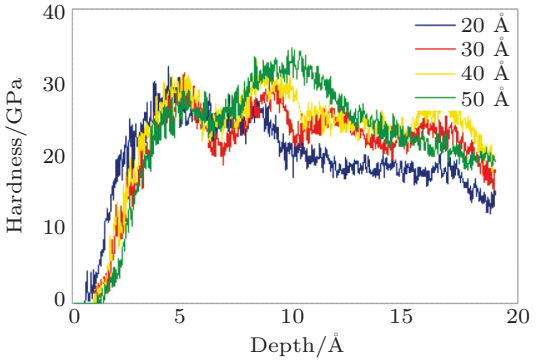


Fig. 9. (colour online) Hardness versus depth plot to describe the effect of film thickness.

for smaller thicknesses, and as the film thickness increases the mechanical behaviour of the film starts to approach to the behaviour of monolithic material.

6. Summary

In the present work the mechanical behaviour of the bilayer film/substrate system is elucidated. For this purpose, first of all, we perform the nanoindentations of monolithic Ni substrate along (100), (110), and (111) planes. It is observed from the results that the mechanical behaviour of monolithic material is independent of the crystalline orientation. Secondly, we choose three bilayer film/substrate systems with heterogeneous interfaces namely Ni(100)/Cu(111), Ni(110)/Cu(111), and Ni(111)/Cu(111) respectively. It is found that interface has a significant effect on the mechanical behaviour of the film, which depends on the degree of lattice mismatch of each layer with the Cu(111) layer. Hence the interface with larger mismatch is softer and *vice versa*. In order to build a relationship between film thickness and effect of interface we choose the Ni(111)/Cu(111) system with thickness values ranging from 20 Å to 50 Å. Mechanical behaviour of the material is characterized by observing the load–depth and hardness–depth curves. It is found that the interface is significant only for the relatively small thickness of film, and the separation between interface and the indenter tip. So an increase in the film thicknesses can cause the mechanical behaviour of the film to shift more towards that of monolithic material.

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