Viscoelasticity of stepped interfaces

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Viscoelasticity of stepped interfaces

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Using molecular dynamics modeling, we show that interfaces in sputter deposited Cu-Nb superlattices exhibit time-dependent elasticity, i.e., viscoelasticity, under shear loading. In the high temperature and small strain rate limit, the interfacial shear modulus approaches a value proportional to the density of steps in the interface. It may therefore be possible to tailor the low-frequency shear moduli of interfaces by controlling their step densities. \copyright 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4827103]

Although they are sometimes viewed as no more than dividing surfaces between neighboring constituents, solid-state interfaces, in fact, have distinct physical properties of their own. Much effort has been devoted to elucidating these state interfaces, in fact, have distinct physical properties of dividing surfaces between neighboring constituents, solid-phase interfacial elasticity,\textsuperscript{5–7} we depict our model dimensions, these strains are approximate to it. Since the Cu and Nb crystals are incommensurate in the interface plane, they must be strained to impose PBCs. For any given temperature and strain rate, interfacial shear moduli are a function of the properties of the constituent materials alone. However, as \( \lambda \) decreases, interfaces between constituent layers have an increasingly important effect on the properties of the superlattice. Thus, interface properties—including elastic constants—may be deduced from the variation of superlattice properties with \( \lambda \).

Our work is motivated by a series of experiments that characterized interfacial elasticity in one-dimensional vapor-deposited Cu-Nb superlattices.\textsuperscript{9,10} Interfaces in sputter-deposited Cu-Nb superlattices form along crystallographic close-packed planes in the neighboring materials, i.e., \{111\} Cu and \{110\} Nb. Additionally, \{110\} Cu is parallel to \{111\} Nb in the interface plane, consistent with the Kurdjumov-Sachs orientation relations.\textsuperscript{11} Such Cu-Nb interfaces exhibit multiple distinct atomic-level structures with nearly equal energies, the most commonly investigated of which are termed KS\textsubscript{1}, KS\textsubscript{2}, and KS\textsubscript{min}.\textsuperscript{12,13} KS\textsubscript{1} is formed by simply joining Cu and Nb crystals according to the crystallography described above. KS\textsubscript{2} is created through a special strain and rotation of a single Cu layer in the KS\textsubscript{1} interface, while KS\textsubscript{min} is realized by removing atoms from either the KS\textsubscript{1} or KS\textsubscript{2} structures until the energy is minimized. Our investigations focus on KS\textsubscript{1}. However, we believe that our conclusions are also applicable to KS\textsubscript{2} and KS\textsubscript{min}, as discussed later.

We constructed an atomic model of a KS\textsubscript{1} Cu-Nb superlattice by imposing periodic boundary conditions (PBCs) on a Cu-Nb bilayer. Our simulation cell has dimensions 97.3 \( \times \) 97.1 \( \AA \) along the interface and 84.2 \( \AA \) perpendicular to it. Since the Cu and Nb crystals are incommensurate in the interface plane, they must be strained to impose PBCs. For our model dimensions, these strains are \( \varepsilon_{\text{Cu}} = -0.0015 \), \( \varepsilon_{\text{Nb}} = 0.00095 \) in the x-direction (\{110\} Cu) and \( \varepsilon_{\text{Cu}} = -0.0026 \), \( \varepsilon_{\text{Nb}} = 0.0013 \) in the y-direction (\{112\} Cu). Initially, we constructed our model with an atomically flat interface. For some simulations with stepped interfaces, we doubled the size of the model in the y-direction without modifying the aforementioned strains.

All simulations were carried out with MD in LAMMPS\textsuperscript{14} using an embedded atom method (EAM) Cu-Nb potential.\textsuperscript{15} The model was annealed at 300 K for \( \sim 10 \) ps and then quenched to 0 K by imposing 5 K decrements every \( \sim 0.5 \) ps. Constant zero stress was maintained using the Nose-Hoover algorithm.\textsuperscript{16} This relaxed structure was prepared for non-zero temperature simulations by ramping the temperature up to the desired value using a similar procedure. Shear strains were applied in the interfacial \{112\} Cu direction by imposing uniform displacement gradient increments upon atomic positions and the simulation cell, followed by MD relaxation at fixed temperature and cell shape for a duration corresponding to the desired strain rate.

Fig. 1(a) shows that the shear response of a flat interface for temperatures ranging from 10 K to 130 K and strain rate \( \dot{\varepsilon} = 5 \times 10^9/\text{s} \) is approximately elastic-perfect plastic. Similar behavior was found for other strain rates, as well. For any given temperature and strain rate, interfacial shear
resistance was determined by averaging shear stress over a strain window of 0.03–0.1. Fig. 1(b) shows how the shear resistance of a flat Cu-Nb interface varies with temperature and strain rate. For 0 K and high strain rate, the shear resistance approaches 0.7 GPa, in agreement with previous studies. However, as the temperature increases, interfacial shear resistance drops rapidly, with lower strain rates giving steeper reductions in shear resistance with increasing temperature. At room temperature, interfacial shear resistance reaches essentially zero for strain rates as high as $5 \times 10^7$/s. Similar results were obtained for Cu-Nb interfaces with $K_{S2}$ and $K_{S\min}$ configurations.

Investigating changes of Cu-Nb interface structure during shearing, we find that interfacial shearing proceeds through localized, thermally activable shear transformations, similar to those described by Wang et al. By analogy to viscous flow in amorphous solids, we model these transformations as an ensemble of two-state systems whose energy landscape may be biased towards one state by an applied stress. The steady state shear resistance $\sigma$ given by such a model is:

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon}_0 e^{-E_a/k_b T} \sinh[\sigma V/k_b T].$$

We fitted this expression to the low temperature, high stress portion of the data in Fig. 1(b) and found an activation energy for the transformations of $E_a = 0.048$ eV, activation volume $V = 11$ Å$^3$, and maximum strain rate $\dot{\varepsilon}_0 = 4.6 \times 10^9$/s. Assuming negligible interactions between neighboring interfaces, the strain rates $\frac{d\varepsilon}{dt}$ in Fig. 1 may be rescaled to arbitrary $\lambda$ as $\frac{d\varepsilon}{dt} = \frac{84\lambda}{\dot{\varepsilon}_0} \frac{d\varepsilon}{dt}$.

This finding has important implications for determining interfacial elastic moduli. Because their elastic limit in shear is essentially zero at room temperature and at experimentally accessible strain rates, atomically flat Cu-Nb interfaces are expected to have zero shear modulus in this regime. Similar conclusions were obtained previously for isothermal (low frequency) elastic shear moduli in theoretical Lennard-Jones superlattices.

However, interfaces in real Cu-Nb superlattices are not atomically flat: they have a slight waviness that may be readily observed in transmission electron microscopy (TEM).

This waviness is likely due to atomic-level interface steps (sometimes referred to as “disconnections” separated by flat terraces. Thus, as a simple improvement of our initial model, we investigate the shear moduli of interfaces containing regularly spaced atomic steps. We created straight linear steps along $\langle 110 \rangle$ Cu by carving out one atom-thick sections of one of the adjacent crystals and filling in these regions with an atom layer from the other crystal. Steps were paired such that for every upward step there is one downward step. Step density, $\delta$, is defined as one over the average distance between successive steps.

With the introduction of steps, the flow stress converges to non-zero values for decreasing strain rate at fixed temperature, at least within simulation times accessible in MD. Thus, elastic constants may be found for interfaces containing steps. For this calculation, we applied cyclic loading: a total shear strain of 0.007 was applied in one direction and then reversed to $-0.007$. With this strain amplitude, all simulations remain below the elastic limit of the stepped interface. Five such straining cycles were performed in each of a sequence of simulations carried out at different temperatures, but with a single strain rate of $7.0 \times 10^7$/s. The shear modulus at each temperature was determined from a linear fit to the quasielastic regions of the resulting stress-strain curve, omitting the first cycle.

Fig. 2 shows the shear modulus as a function of temperature for an interface with step density $\delta = 0.0205$/Å. The fitted modulus is temperature dependent and decreases from a value of $\sim 35$ GPa near 0 K to an asymptotic value of $\sim 16$ GPa above 150 K. The insets in Fig. 2 show interface stress-strain curves at 10 K, 90 K, and 290 K. Each of these insets illustrates distinct responses of the interface to cyclic loading. At low temperature, the interface is strictly hyperelastic, meaning that the shear modulus may be determined directly from the strain energy stored in stretched bonds at the interface. In the temperature range of $\sim 50–150$ K, the interface is viscoelastic: in addition to contributing to elastic strain energy, some of the work done during each straining cycle is dissipated by thermally activated relaxations at the interface, as evidenced by the hysteretic stress-strain response. Finally, at temperatures above 150 K, this hysteretic response vanishes because all thermally activated stress relaxations occur fast enough to remain in equilibrium with...
Here, \( f \) is the volume fraction associated with the interface elastic constant, \( C_{\text{int}} \), while the remainder of the system has a bulk elastic constant, \( C_{\text{bulk}} \). Using standard composite theory, we compute the elastic constant \( C_{\text{bulk}} \), characteristic of a superlattice in the large \( \lambda \) limit. \( C_{44} \) refers to the relaxed modulus obtained by MD. Using standard composite theory, we compute \( C_{\text{bulk}} \approx 40.3 \text{ GPa} \). We estimate \( f \) by taking the interface region to consist of one atomic layer on each side of the interface, giving \( f = 0.16 \).

We computed \( C_{\text{int}} \) for four different \( \delta \) values and found that it increases monotonically with \( \delta \), as shown in Fig. 3. At low \( \delta \), \( C_{\text{int}} \) varies roughly linearly with \( \delta \) with a best-fit slope of 269 GPa Å. This behavior likely arises because, at sufficiently high temperatures and low strain rates, tractions along the flat terraces between steps relax to zero, as in the case of atomically flat interfaces. The steps are then the only parts of the interface that bear loads and each may be viewed as an independent linear spring. The total elastic response of the interface consists of the individual step springs in parallel, since each step has the same strain. This means that \( C_{\text{int}} \) scales directly with \( \delta \), if each step is independent. There is a departure from this trend for high \( \delta \), which may arise from interactions between steps. Extending this view to lower temperatures and higher strain rates, the elastic response of the interface may be described by a complete Maxwell model consisting of a spring parallel to another spring in series with a dashpot. Such models have been extensively used to describe viscoelasticity in polymers and, properly parameterized, also reproduce the interface behavior illustrated in Fig. 2.

Experiments on Cu-Nb superlattices inferred shear elastic constants from surface shear wave velocities measured using Brillouin scattering at room temperature. Generally, this type of experiment is assumed to measure high frequency elastic constants on time scales much faster than viscous processes in the system and previous theoretical works have made this assumption. Based on the frequency (~5 × 10^9 GHz) and speed (~2 × 10^3 m/s) of shear waves in these experiments, we estimate their wavelengths to be ~4 × 10^3 Å, which is much greater than the superlattice period. Therefore, strains may be considered approximately uniform over several bilayers, meaning that the experiment measures composite average elastic constants.

Although it is difficult to calculate the strain rate during Brillouin scattering exactly, a conservative estimate might assume a maximum strain amplitude of 0.01 (beyond this strain, the elastic behavior of the material is likely non-linear). Then, experiments that measure phonons with a frequency of 5 × 10^9 GHz would have a maximum strain rate of order 10^3/\( \text{s} \). According to Fig. 1, this upper bound falls somewhat short of the asymptotic limit where, at room temperature, the shear resistance on flat interface terraces reaches zero. However, since the shear resistance at this temperature and strain rate is around 10% of the shear resistance in the zero temperature limit, the shear moduli measured in Brillouin scattering experiments are likely to be close to the relaxed modulus values describe above.

Assuming that the Brillouin scattering experiments measure relaxed moduli, we can make an estimate for the step density based on our model using available experimental data. The experiments found a ~5%–8% decrease in the shear velocity at \( \lambda \approx 84 \text{ Å} \), compared to the large \( \lambda \) limit, indicating \( C_{\text{int}} \approx 0.45 C_{\text{bulk}} \approx 18 \text{ GPa} \) and therefore \( \delta \approx 0.067/\text{Å} \). This estimate is likely an upper bound because it was found using the low-\( \delta \) linear fit, which underestimates \( C_{\text{int}} \) for \( \delta \approx 0.067/\text{Å} \). Furthermore, we have ignored several important factors in this calculation, such the anisotropy of interface shear response, the real morphology of interfacial steps (which are unlikely to be perfectly linear), and the crystallographic texture of the sputter deposited Cu-Nb superlattice. The outcome should therefore be viewed as qualitative.

Our simulations predict that the shear elastic constants of interfaces in Cu-Nb superlattices are highly temperature dependent.
dependent. Cryogenic measurements of shear elastic constants may be able to validate this prediction. The most significant parameter influencing relaxed shear elastic constants is not interface structure or bond strength, but interface step density, δ. Therefore, our findings cannot be described as either “superlubricity” or as a “supermodulus” effect. In the high temperature and low strain rate limit, it may be possible to influence interface elastic constants by changing δ, e.g., through control of interface crystallography. For instance, Cu-Nb interfaces created by severe plastic deformation with the same orientation relation but different interface plane orientations than those discussed here have an atomically rough structure in one direction. They may therefore have higher shear stiffness in that direction. By contrast, interfaces synthesized through molecular beam epitaxy (MBE) may have lower stiffness on account of their near perfect flatness.

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20See supplementary material at http://dx.doi.org/10.1063/1.4827103 for a derivation of this expression.


24A. G. Every, NDT & E Int. 27(1), 3 (1994).

