Investigation of multilayer relaxation on Al(110) with the use of self-consistent total-energy calculations

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The geometry of the Al(110) surface is determined with the use of first-principles self-consistent total-energy calculations. Use of the Hellmann-Feynman theorem to calculate forces allows the determination of the equilibrium atomic positions with a small number of trial geometries. The calculated results agree well with the low-energy electron diffraction measurements and the physical mechanism behind the oscillatory multilayer relaxation is discussed.

INTRODUCTION

The first and foremost question in surface science concerns the location of the atoms at the surface. Atoms near the surface of a crystal are under the influence of different forces from those in the bulk, and in most cases relaxations or reconstructions of the bulk lattice will occur in the topmost layers. Such changes in geometry can have significant effects on the physical properties of the metal surface (e.g., changes in work functions, reactivities, etc.). Although a great deal of progress has been made, the geometries of many well-studied surfaces still remain uncertain.¹

Previous studies have shown that first-principles totalenergy calculations using local-density-functional formalism are very successful in determining structural and vibrational properties of a large variety of bulk materials²⁻⁴ and it has just become feasible to apply these techniques to study surface structures. Up to now, most of the effort has been devoted to semiconductor surfaces.^{5,6} For metals, the necessity of accurately representing electronic states near the Fermi level requires sampling more grid points in the surface Brillouin zone and it is only very recently that total-energy calculations have been attempted for realistic metal surfaces.^{7,8} So far structure determination for metal surfaces is restricted to one investigation on the W(100) surface.⁸ We present here a study of multilayer relaxation on the Al(110) surface using firstprinciples self-consistent total-energy calculations. The choice of Al(110) was motivated by the existence of detailed experimental studies [low-energy electron diffraction (LEED)] and the big relaxations reported for this surface.9,10

Recent experiments⁹⁻¹² have indicated that for a large number of surfaces the change in bulk geometry is not restricted to the topmost layer but oscillatory relaxations of the interlayer distances occur for several layers into the bulk. The existence of oscillatory multilayer relaxations on metal surfaces was first suggested by the results from model calculations.¹³ However, although the qualitative features of the relaxation are model independent, the magnitude of the relaxations is very sensitive to details of the models: In particular, the three-dimensional aspect of the electron density and treatment of the electronic screening showing the importance of a realistic fully self-consistent treatment of the electrons at the surface.

From our calculations we find a contraction of the top interlayer spacing by $6.8\pm0.5\%$, an expansion of the second interlayer spacing by $3.5\pm0.5\%$, and contraction of the third interlayer spacing by $2.0\pm0.5\%$, in agreement with experiment.^{9,10} Unlike the previously reported case of W(100),⁸ we find that the forces acting on the Al(110) surface are of longer range and a slab of 13 to 15 layers thick is necessary to obtain reliable results.

CALCULATION

Self-consistent pseudopotential calculations are performed for the Al(110) surface using the periodic slab geometry. Slabs of thickness up to 15 layers are used separated by at least five layers of vacuum. For a given trial geometry, the total energy of the system is calculated within the local-density-functional formalism¹⁴ using the Wigner interpolation formula¹⁵ for the electronic exchange and correlation. The norm-conserving pseudopotential¹⁶ in the present calculations has been used in previous calculations of the bulk structural properties² and phonon frequencies³ of Al with excellent results. In our calculations, plane waves with kinetic energy up to $E_1 = 8.5$ Ry are used in the expansion of the electronic wave functions and plane waves with energy up to $E_2 = 12.0$ Ry are included with second-order perturbation. Calculated bulk properties are in good agreement with previous calculation² and experiment. Sampling grids for the surface calculations vary from 35 to 140 points in the irreducible region of the surface Brillouin zone. Partial occupancy of states near the Fermi level are taken into account by a Gaussian smearing scheme which broadens each energy level and calculates the Fermi energy and fractional occupation for each state from the resultant density of states. This scheme has proven to be very useful in previous calculations.¹⁷

In addition to the total energy, the forces exerted on each atomic layer are calculated using the Hellmann-Feynman (HF) theorem.¹⁸ The use of HF forces minimizes the number of trial geometries needed to determine the equilibrium geometry especially when a number of layers are relaxed simultaneously. We have tested the accuracy of our calculated HF force by shifting the top layer and calculating the total-energy difference. Forces deduced by the two procedures agree to better than 1.5×10^{-4} Ry/a₀ corresponding to an uncertainty of less than 0.1% in the interlayer spacing (~ 0.003 Å). The agreement for the inner layers are even better. The adequacy of the vacuum spacing between slabs is tested by performing calculations for two similar slabs with spacings of five and nine layers. The forces calculated for the two cases differ less than 3×10^{-4} Ry/ a_0 (~0.2% in the interlayer spacing). Increasing the basis set size by changing E_1 to 11.0 Ry and E_2 to 15.5 Ry changes the force on the top layer by less than 3×10^{-4} Ry/ a_0 (~0.2% in the interlayer spacing). Effects of changing the sampling grid and the thickness of the slabs are discussed in detail below. Accurate calculation of the HF forces imposes stringent requirements on self-consistency; in our calculations a dielectric matrix scheme¹⁹ is used to accelerate convergence. Iteration is carried out until the HF forces are stable to within 5×10^{-5} Ry/ a_0 . Using the forces calculated from the first few geometries, a force-constant

matrix coupling the different layers is deduced which is then used to guide further changes in geometry. Different geometries are tried until the forces on every layer drop below 1.5×10^{-3} Ry/ a_0 .

RESULTS

Detailed tests are carried out to test the dependence of our results on the number of slab layers and the number of grid points sampled in the surface Brillouin zone (SBZ). The results are summarized in Table I which lists the changes in interlayer spacings in the top five layers for the cases we have tested. Results in the first three columns are obtained using a Gaussian smearing of 0.05 eV for Fermi-surface weighting. Except for the cases marked by asterisks, these correspond to "zero force" geometries (with the criterion specified above). The other cases are approximate geometries deduced by using the force constant matrix. The interlayer spacings show an oscillatory convergence with an increase in the number of slab layers and grid points. The slow convergence with the number of grid points is probably due to the inadequate sampling of surface states which exist near the Fermi level in a small region around the S points in the SBZ. We found that increasing the Gaussian smearing to 0.20 eV allows us to obtain convergent results with a smaller grid (see the fourth column in Table I). The oscillatory convergence with the slab thickness is caused by interaction between the two surfaces of the slab. This problem is greatly aggravated by inadequate Fermi-surface sampling. We find that the slab must be at least 13 layers thick to obtain reasonably converged results. From our results, we deduce that on the Al(110) surface $d_{12} = -6.8 \pm 0.5\%$,

TABLE I. Convergence of multilayer relaxations on Al(110) as a function of slab thickness and size of the sampling grid. The first three columns use a Gaussian smearing width of 0.05 eV for Fermisurface weighting (except for the cases marked by asterisks, these correspond to zero-force geometries) and the last column uses an increased value of 0.20 eV for the smearing width.

		Number of k points			
	Number of layers			• ·	
	in slab	35	70	140	35
9	Δd_{12}	-6.6*	-5.6*	-6.0*	
	Δd_{23}	+ 3.1	+3.1	+ 3.1	
	Δd_{34}	-1.5	-1.0	-1.3	
	Δd_{45}	+ 1.8	+ 2.4	+ 2.1	
11	Δd_{12}	-9.3*	-8.8	-8.7	8.4*
	Δd_{23}	+ 4.6	+3.8	+ 4.1	+ 3.9
	Δd_{34}	-3.1	-2.9	-3.0	-2.4
	Δd_{45}	+ 0.7	+ 0.8	+ 0.9	+0.5
13	Δd_{12}	-7.7*	-6.2	-6.7	-6.9
	Δd_{23}	+ 4.2	+3.5	+3.7	+3.5
	Δd_{34}	-3.4	-1.4	-1.5	-2.0
	Δd_{45}	+ 0.8	+ 1.8	+ 1.5	+ 1.8
15	Δd_{12}	- 5.9	-6.8	7.0	-6.8
	Δd_{23}	+2.8	+3.6	+ 3.4	+ 3.5
	Δd_{34}	-2.3	-2.2	-2.4	-2.4
	Δd_{45}	+ 1.6	+ 1.6	+ 1.6	+ 1.5

		Calculated	Expe	eriment	
Surface energy					
(eV/surface atom)		0.77 ± 0.02	0.	.81ª	
(ergs/cm ²)		1090 ± 30	11	180 ^a	
Work function (eV)	4.32			4.28 ^b	
	Geometry (relaxation in % of interlayer separation)				
	Calculated	Ref. 9	Ref. 1	10	
Δd_{12}	-6.8 ± 0.5	-8.5 ± 1.0		-0.8	
Δd_{23}	$+3.5\pm0.5$	$+ 5.5 \pm 1.5$	$+ 5.0 \pm$	1.1	
Δd_{34}	-2.0 ± 0.5	$+2.4\pm1.6$	$-1.6\pm$	1.2	
Δd_{45}	$+ 1.6 \pm 0.5$				

TABLE II. Comparison of calculated results with experiment.

^aReference 21.

^bReference 22.

 $d_{23} = +3.5 \pm 0.5\%$, $d_{34} = -2.0 \pm 0.5\%$, and $d_{45} = +1.6 \pm 0.5\%$. A comparison of our results with experiment is given in Table II. The agreement between theory and experiment is quite good. The discrepancy in d_{12} is a bit larger than the quoted errors and might be attributed to systematic errors which can come from the analyses of the LEED data (for example, the assumption of a bulk potential for the surface atoms) or from the calculation due to corrections to the local-density approximation for electronic exchange correlation at the surface.

Detailed results for the work functions and surface energies are summarized in Table III. The work function is much less sensitive to the slab thickness and the sampling grid than the layer relaxation. In the calculation of surface energies, the bulk energy is evaluated by replacing the vacuum layers in the unit cell with bulk layers and using a sampling grid compatible with the surface calculation for best cancellation of errors. This method gives more stable results than the method of evaluating the bulk energy by subtracting two surface calculations. See Table II for comparison with experiment. The energy associated with the multilayer relaxation is about 10 meV, which is only a small fraction of the total surface energy. We find only a small change in work function ~ 0.2 eV between the relaxed and ideal surfaces.

TABLE III. Variation of calculated surface energies and work functions with slab thickness and sampling grid.

Surface energy (eV/surface atoms)					
Size of sampling grid	9 layers	11 layers	13 layers	15 layers	
12	0.73	0.80	0.76	0.77	
35	0.76	0.78	0.78	0.78	
7 0 ·	0.75	0.78	0.75	0.76	
140	0.75	0.79	0.75	0.77	
	,	Work function	(e V)		
а	4.39	4.28	4.33	4.32	

^aThe work function for the case of 35, 70, and 140 k points are all within ± 0.01 eV of one another.

DISCUSSION

In order to understand better the physical mechanism behind the oscillatory relaxations, we have also calculated the interplanar forces for the unrelaxed geometry. The results are shown in Table IV. The forces on the top few layers alternate in sign and correlate quite well with the final relaxations. For comparison, the second column in Table IV shows the forces obtained from a model of point ions in a truncated uniform background, which also shows the same sequence of oscillatory forces but with vastly different magnitudes and rate of decay into the bulk. The basic origin of the force oscillation lies in the alternating stacking sequence of the layers at the (110) surface of the fcc lattice (see the Appendix). The third column shows the forces obtained by replacing the truncated uniform profile with a one-dimensional charge profile obtained by averaging the calculated charge density parallel to the surface. We can see that the difference in magnitudes between the point-ions flat-background model and the full calculation is not caused by charge leaking out from the first layer into the vacuum. The main cause for the difference arises from the variation of the electron density in directions parallel to the surface because of the ion potentials. Figure 1 shows the electron distribution in the [001] and [111] planes perpendicular to the surface for

TABLE IV. Calculated forces on atomic layers in the unrelaxed geometry. Positive value indicates direction of force is towards the surface. Negative value indicates force is directed into the bulk.

Force (mRy/a_0)						
Layer	Full calculation	Model 1 ^a	Model 2 ^a			
1	-6.76	-518.15	-462.25			
2	+ 6.20	+75.82	+ 76.48			
3	-0.88	-6.77	-7.72			
4	+3.53	+0.72	+ 0.69			
5	+2.43	-0.08	+0.75			
6		+ 0.01	-0.10			
7	-3.14	-0.00	-0.13			

^aSee the text.



FIG. 1. Contour plots of the valence charge density at the unrelaxed (110) surface of Al in two planes perpendicular to the surface. The positions of atoms are indicated by solid circles. The unit of charge density is in electrons per unit cell volume.

the unrelaxed surface. It can be seen that there is a clumping up of electrons directly on top of each of the surface atoms. This gives rise to an outward force on the first layer which counterbalances the force produced by the ions. The importance of including the three-dimensional character of the electronic charge density is also emphasized in previous investigations.¹³ The difference in decay rates indicates the contribution of forces mediated by itinerant electrons which shows a longer range than the simple direct ion-ion interaction. The effects of these forces can be seen in phonon-dispersion curves (where Born—von Kármán analysis indicates the presence of forces up to eight nearest neighbors²⁰) and in the necessity of using a thicker slab to decouple the two surfaces in our calculations.

In the unrelaxed geometry, the charge density between the atoms are fairly uniform and we find no evidence of the "backbonding" effect (due to rehybridization of broken surface bonds) which is important for structural reorganization on semiconductor surfaces. This is changed in the relaxed geometry where there is a noticeable increase in charge between the top layer atoms and their surrounding atoms (see Fig. 2). This leads to a strengthening of the surface force constants coupling the top layer surface atoms. By calculating the forces exerted on the different



FIG. 2. Valence charge density at the Al(110) surface after relaxation.

layers when the geometry is slightly disturbed from the force-free situation, we obtain force constants coupling the different layers. Our results show that the surface force constants coupling the top layer of atoms can be enhanced by as much as 20%. We have used these first-principles derived surface constants to calculate the surface phonon dispersion on the Al(110) surface. Details of these calculations will be published in a coming paper.

SUMMARY

In conclusion, we have used first-principles selfconsistent total-energy calculations to investigate successfully the surface structure of the Al(110) surface. Detailed tests have been made to ascertain the reliability of the method and we anticipate rapid developments in applications to other surfaces in the near future.

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APPENDIX

In this appendix, we will go through a heuristic argument to illustrate how the pattern of the oscillatory relaxation is related to the stacking sequence of the layers at the surface. Consider the electric field of a layer of positive ions in a slab of uniform neutralizing background. Consider the electric field outside such a slab: Because of the neutrality of the slab, the total electric flux through any plane surface outside the slab must vanish. This means the electric field must be oscillatory in space in directions parallel to the layer and, moreover, these oscillations decay exponentially with the distance from the slab. Thus in a case where the layers are stacked in an alternate sequence ABABAB..., A and B layers will attract each other while A - A and B - B will be repulsive. When half of the solid is removed to form a surface the electrical forces on the surface layers are dominated by the first missing layer because of the exponential decay of the fields. Thus the forces on the first, third, and fifth layers will be directed into the surface because of the loss of the attraction to the removed layer while the forces on the second, fourth, and sixth layers will be directed towards the surface because these layers were originally repelled. This will produce the observed damped oscillatory pattern in the relaxations at the surface. Extending the above arguments to ABCABC... type of stacking for the (111) faces of fcc metals leads to patterns $--+-+\cdots$ for the interlayer spacings. The decay length of the electric fields away from the surface is equal to the spacing of ions in the layers, thus we can also understand qualitatively why relaxations for close-packed faces are smaller than open faces.

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