Oscillatory Nonmetal-Metal Transitions of Ultrathin Sb Overlayers on a GaAs(110) Substrate

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Based on first-principles calculations, an Sb film on GaAs(110) is found to be nonmetallic at 1 and 3 monolayer (ML) coverages, and metallic at 2, 4, and higher ML coverages. These unusual oscillatory nonmetal-metal transitions are explained in terms of a generalized Wilson rule, constrained by the relative magnitudes of the separation and width of the subbands derived from the quantum-well states. The present study also establishes the existence of magic stability of the film at the odd numbers of monolayers, and strong interlayer spacing oscillations. [S0031-9007(98)05878-5]

Metallic overlayers on semiconductor substrates consist of an important class of heteroepitaxial growth systems. In such systems, the common growth mode is by the formation of three-dimensional (3D) islands on top of a few or zero wetting layers, leading to rough films [1–3]. However, controlled manipulation of the growth processes can result in the formation of flat metal films, as demonstrated in a recent study of Ag growth on GaAs(110) [4]. Here atomically flat silver films have been obtained, but only if the film thickness is above some critical thickness. This striking observation of the existence of such a reversed critical thickness has motivated the development of a phenomenological growth model [5], showing that the confined motion of the conduction electrons can be important in the stabilization of many metal overlayers on various substrates. Within this model, a metal film of any thickness can be stablized by quantum confinement, while it can also be destablized by charge spilling from the metal to the substrate; their competition may define the critical thickness as observed. Several earlier theoretical studies have also explored various different manifestations of quantum size effects in either freestanding metal films [6] or metallic overlayers on metal substrates [7].

As a prototype nondisruptive metal-semiconductor interface system, the growth of Sb on GaAs(110) has also been investigated extensively [8–14]. Based on Auger electron spectroscopy [8] and scanning tunneling microscopy (STM) studies [9,10], the growth pattern of Sb has been found to follow a $(1 + M)$ mode (or a modified Stranski-Krastonov mode): a monolayer followed by sets of multilayers of a well-defined thickness M (see Fig. 1). Moreover, I-V measurements showed that the band gap at the Fermi energy decreases with increasing film thickness, suggesting a nonmetal-metal transition at a higher coverage [10]. Theoretically, most previous studies have concentrated on the adsorption of 1 monolayer (ML) Sb on GaAs(110) [11–14]. Our present study of the system in the multilayer regime aims in providing the physical insights into the understanding of those growth phenomena.

In this Letter, we present what seems to be the first investigation of quantum size effects in the model system, Sb/GaAs(110), within the first-principles density-functional theory. In our calculations, the effects of quantum confinement and charge spilling are treated self-consistently, with inclusion of surface relaxation. We find strong manifestations of quantum size effects, in both known and unexpected ways. As the film thickness increases, the adsorption energy per layer oscillates, thereby defining the existence of magic thicknesses for smooth growth. This finding provides the microscopic basis for the $(1 + M)$ growth mode. Furthermore, there exist corresponding oscillatory nonmetal-metal transitions, a surprising finding in contradiction with traditional belief. We identify the underlying physical
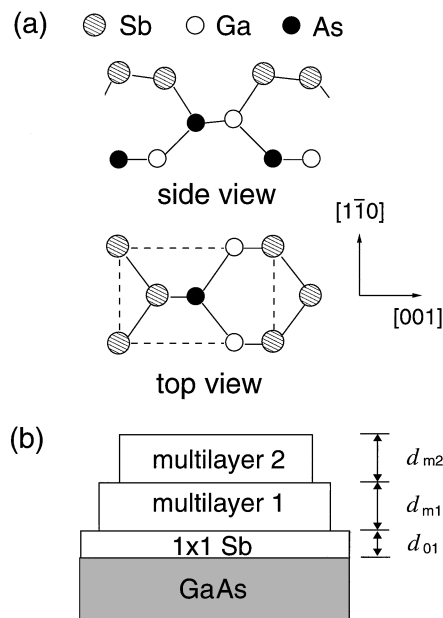

FIG. 1. (a) Schematic diagrams of the side and top views of the epitaxial continued layer structure model for the 1 ML-Sb/GaAs(110)-(1×1) system. (b) Schematic cross-sectional view depicting Sb multilayers on the GaAs(110) substrate.

reasons for the existence of the oscillatory nonmetal-metal transitions, discuss the results in comparison with existing experiments, and suggest new ways to test some of the unique predictions made here.

In our calculations, we use norm-conserving separable pseudopotentials [15,16] together with the density-functional theory within the local-density approximation (LDA) [17,18]. Partial-core corrections are included in the pseudopotentials of Ga [19]. We model the Sb/GaAs(110) system by a periodic slab geometry. Each slab contains seven GaAs substrate layers and a certain Sb overlayer on each side of the slab. The vacuum region between such slabs has a thickness of about 10 Å. The Sb overlayer is modeled by the so-called epitaxial continued layer structure [12–14], where the Sb atoms grow epitaxially in the form of zigzag chains in the $[1\bar{1}0]$ direction on a nearly bulklike GaAs(110) substrate (see Fig. 1). To optimize the atomic structure, atoms in the overlayer and the substrate are relaxed along the calculated forces until the remaining forces are all within 6 mRy/Å. We employ a plane-wave basis with an energy cutoff of 10 Ry and take a uniform grid of 24 **k** points within the (1×1) surface Brillouin zone. The calculation scheme and its previous application to the Sb monolayer on GaAs(110) are described in detail elsewhere [14].

In order to examine the relative stability of Sb adsorption on GaAs(110) with increasing Sb coverage, we calculate the adsorption energy (E_{ad}) per Sb atom from

$$E_{ad} = [E(n-1) + 4E_{Sb}^{a} - E(n)]/4, \quad (1)$$

where $E(n-1)$ and $E(n)$ are the total energy for a slab with the Sb coverage, θ, equal to $(n-1)$ and n ML, respectively, and E_{Sb}^{a} is the total energy of a free Sb atom. In the case of $n = 1$, $E(n-1)$ corresponds to the total energy of the clean GaAs(110) surface. The negative of the adsorption energy with respect to the Sb coverage is plotted in Fig. 2, showing strongly oscillatory size effects: The adsorption energies at $\theta = 1$, 3, and 5 ML are larger than those at 2 and 4 ML. This energetic information indicates that the first Sb monolayer, at which
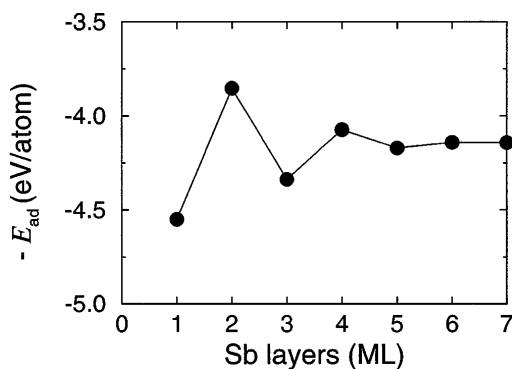
the adsorption energy is the largest, binds most strongly to the GaAs substrate. A flat film at $\theta = 3$ or 5 ML is locally stable, but a flat film at 2 or 4 ML is unstable against roughening. Therefore, one expects Sb growth on GaAs(110) to follow the $(1 + M)$ mode, with $M = 2$. This finding qualitatively explains the experimentally observed $(1 + M)$ growth mode in this system. However, we note that on a quantitative level earlier experiments suggested M to be 3, estimated by using the constant bulk interlayer spacing for the Sb thin films [9,10]. As shown below, this discrepancy can be resolved by considering the large deviations of the interlayer spacings in the Sb thin films from the bulk value. Figure 2 also shows that the adsorption energy changes little above 6 ML of Sb; therefore, the double layer growth mode will no longer be favored at such higher coverages.

In Table I, we summarize the calculated interlayer spacings of the Sb overlayers. It is worth emphasizing the following aspects: (i) The topmost Sb-Sb interlayer spacing varies with the film thickness in an oscillatory way, taking the values of 2.94, 2.77, 2.88, 2.79, and 2.81 Å as θ increases from 2 to 6 ML. After 6 ML the oscillation disappears. Such variations in the topmost interlayer spacing should be observable, for example, by measuring the height of sizable monolayer-high islands formed at the growth front, as reported in a recent experimental study of Pb/Ge(100) [20]. (ii) For a given coverage, the interlayer spacing also oscillates from layer to layer.

The present results for the heights of double Sb layers (d_{m1} and d_{m2} in Fig. 1) are given in Table II together with those from experiments [9,10]. The values of $d_{m1} = 6.2$ Å and $d_{m2} = 6.0$ Å are in good agreement with the STM measurements of Shih, Feenstra, and Mårtensson [9] ($d_{m1} = 6.0 \pm 0.5$ Å and $d_{m2} = 6.0 \pm 0.5$ Å) and Patrin et al. [10] ($d_{m1} = 6.4 \pm 0.5$ Å and $d_{m2} = 6.4 \pm 0.5$ Å). However, both STM studies estimated the coverages of the first and the second multilayers to be 4 and 7 ML, respectively, by using the bulk interlayer spacing of about 2 Å. Our calculations show that the interlayer spacings in the thin Sb overlayers are significantly larger than the bulk value (see Table I), a prediction to be confirmed in future experiments.

The oscillatory behavior of the interlayer spacing is a consequence of the quantum size effect. The electronic

FIG. 2. Negative adsorption energy as a function of the Sb coverage.

TABLE I. Calculated interlayer spacings (in Å) for the Sb overlayers on GaAs(110).

	d_{01}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}	d_{67}
1 ML	2.39						
2 ML	2.54	2.94					
3 ML	2.41	3.44	2.77				
4 ML	2.44	3.28	2.99	2.88			
5 ML	2.43	3.25	2.86	3.16	2.79		
6 ML	2.44	3.28	2.87	2.97	3.02	2.81	
7 ML	2.43	3.24	2.89	3.00	2.94	3.08	2.81

TABLE II. Calculated heights (in Å) of Sb multilayers in comparison with experimental results. For the denotations of d_{m1} and d_{m2}, see Fig. 1. The interlayer spacing between the Sb layer and the GaAs substrate (d_{01}) is given for comparison.

	d_{01}	d_{m1}	d_{m2}
Present study	2.4	6.2	6.0
STM I[a]	2.5	6.0 ± 0.5	6.0 ± 0.5
STM II[b]	2.5	6.4 ± 0.5	6.4 ± 0.5

[a]Reference [9] (Shih, Feenstra, and Mårtensson, 1990).
[b]Reference [10] (Patrin *et al.,* 1992).

density in the quantum well has an oscillatory position dependence in the growth direction. It is natural to expect similar adjustment of the ions to minimize the electron-ion interaction energy [6]. Here we like to emphasize only the observation that the amplitude of oscillation is particularly large at $\theta = 3$ ML, when the system is in the nonmetallic state (see below). This can be explained qualitatively by the fact that in the nonmetallic state the charge density fluctuation is associated with one-dimensional screening, while in the metallic state the magnitude of the fluctuation associated with three-dimensional screening is smaller.

We have also obtained the band structures of the system at different Sb coverages, with those at 1 and 2 ML shown in Fig. 3. There are four subbands in the bulk gap at $\theta = 1$ ML [12,13]; the lower two subbands are fully occupied, and the higher ones are empty. Thus
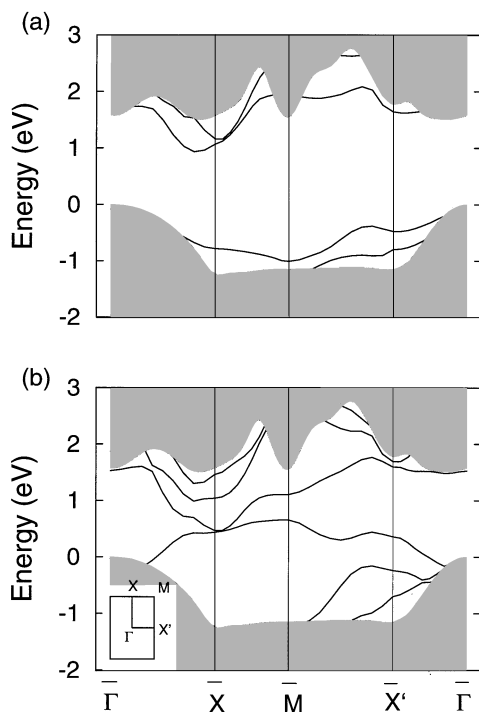

FIG. 3. Surface band structures of Sb/GaAs(110)-(1 × 1) at two Sb coverages: (a) 1 ML; (b) 2 ML. The inset in (b) shows the surface Brillouin zone for the (1 × 1) unit cell.

the 1-ML Sb overlayer is nonmetallic with a band gap of 0.9 eV. The 2-ML Sb overlayer has two additional subbands in the bulk gap, which overlap across the Fermi energy, leading to a metallic state. Surprisingly, these overlapping subbands appear oscillatorily with increasing Sb thickness: They disappear at 3 ML and reappear at 4 ML. As a result, the 3-ML Sb overlayer has a band gap of 0.1 eV, and the 4-ML Sb overlayer shows a metallic state. Above $\theta = 5$ ML the system is always metallic. The calculated band gap with respect to the Sb coverage is summarized in Fig. 4. It is well known that the LDA calculation underestimates the band gap. For example, the experimental band gap at 1 ML is about 1.3 eV [9,10], larger than the calculated value of 0.9 eV. Therefore, we expect that the real band gap at 3 ML is also larger than the present LDA value of 0.1 eV. Because the 2- and 4-ML Sb overlayers show metallic behavior with the presence of the two overlapping subbands at the Fermi energy, they are energetically unstable compared to the 1- and 3-ML Sb overlayers, consistent with the results shown in Fig. 2.

It is remarkable that the Sb overlayers on GaAs(110) show oscillatory nonmetal-metal transitions. For metal overlayers on semiconductor substrates, the typical picture for nonmetal-metal transition is as follows [21]: The overlayer is nonmetallic if the coverage is too low, becomes metallic at some critical coverage, and is expected to be more metallic if additional layers of metal are added. However, in the present study we find that a metallic overlayer at $\theta = 2$ ML will turn into a nonmetallic state if one more layer of Sb is added.

The unusual oscillatory nonmetal-metal transitions can be explained by the classic Wilson rule [22], generalized to the present case, and constrained by the quantum size effect of the thin film. Because the dangling bonds of the topmost Sb layer atoms are fully occupied, we can regard our quantum well to really start at $\theta = 2$ ML. At $\theta \geq 2$ ML, because each Sb atom is tetrahedrally bonded in the (1 × 1) structure, each unit cell of a given Sb layer contains two nearly equivalent "free" electrons. Therefore, the total number of such electrons
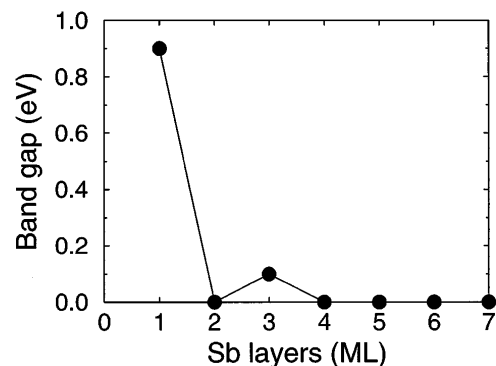

FIG. 4. Band gap as a function of the Sb coverage.

per unit cell of the thin film is always an even number, $2n$, with $n = 1, 2, 3, \ldots$ for $\theta = 2, 3, 4, \ldots$ ML. On the other hand, each additional Sb layer also contributes two overlapping subbands, due to the confinement in the vertical direction. For small enough film thicknesses at which different subbands originated from different Sb layers do not overlap in energy, we expect metal-nonmetal transitions according to a generalized Wilson rule: metal for odd n and nonmetal for even n. Therefore, we have a metallic system at $\theta = 2$ ML, a nonmetal at 3 ML, and a metal again at 4 ML. This oscillatory behavior will stop, however, if the film is above a critical thickness where the spacing between the subbands contributed by neighboring layers becomes smaller than the width of the subbands, because then the different subbands overlap in energy and only the metallic state prevails. Below the critical thickness, we expect that the gap between the filled and empty subbands of the nonmetallic state decreases with the film thickness, as shown in Fig. 4. Based on the above picture, we further infer that oscillatory nonmetal-metal transitions should *not* be expected in alkali metal films on semiconductors, because the subbands associated with those simple metals are typically very broad. On the other hand, for systems of metal overlayers with flatter subbands, oscillatory nonmetal-metal transitions can persist to even higher film coverages.

In summary, our first-principles calculations have shown that, in the model metal/semiconductor growth system of Sb/GaAs(110), quantum size effects can prevail in several dramatic ways. The adsorption energy per layer has been found to oscillate with the overlayer thickness, making flat films at 1, 3, and 5 ML coverages magically stable, and films at 2 and 4 ML unstable. This finding qualitatively explains the $(1 + M)$ growth mode observed in previous experiments, and calls for more precise determination of M in future experiments. For films at different thicknesses, there exist strong oscillations in the topmost interlayer spacings; and for a film of a given coverage, the interlayer spacing within the film should also oscillate from layer to layer. Finally, there should exist oscillatory nonmetal-metal transitions as the film thickness increases, a prediction to be confirmed in future experiments (for example, by locally probing the band gaps using the scanning tunneling spectroscopy). All these oscillatory properties, in the stability, interlayer spacing, and transport, are correlated at the fundamental level.

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