

## Interface phenomena at semiconductor heterojunctions: Local-density valence-band offset in GaAs/AlAs

S. Massidda, B. I. Min,\* and A. J. Freeman

*Materials Research Center and Department of Physics and Astronomy, Northwestern University,  
Evanston, Illinois 60201*

(Received 10 March 1987)

The valence-band offset  $\Delta E_v$  at the lattice-matched GaAs/AlAs(001) interface is derived from highly precise self-consistent all-electron local-density band-structure calculations of the  $(\text{GaAs})_n(\text{AlAs})_n(001)$  superlattices (with  $n \leq 3$ ). We calculate  $\Delta E_v$  by using the core levels—available uniquely from an all-electron approach—as reference energies. Since these are experimentally accessible quantities, a direct comparison with experiment is, in principle, possible. We find that  $\Delta E_v = 0.5 \pm 0.05$  eV, in very good agreement with recent experimental results ( $\Delta E_v = 0.45\text{--}0.55$  eV). Calculated core-level shifts are also compared to experiment. These results, which are closely related to changes in the charge-density distribution at the interface, contribute to understanding the underlying mechanism of the band discontinuity.

In a recent review, Bauer and Margaritondo<sup>1(a)</sup> have emphasized that understanding interface phenomena at semiconductor heterojunctions is essential for the design of novel devices. To this end, a precise knowledge of the band structure and especially of the band alignment at a semiconductor heterojunction—as probably the single most important property of the interface—is necessary. Particular attention has been devoted to the almost perfectly lattice-matched GaAs/AlAs heterojunction, both from the experimental and the theoretical points of view.<sup>2</sup> However, there is still no general agreement regarding the value of, and microscopic mechanism causing, the band discontinuities at this interface. The experimental valence-band offsets ( $\Delta E_v$ ), as measured by several techniques, range<sup>2-5</sup> from 0.19 to 0.65 eV. Until recently, a partitioning of the valence- and conduction-band gap contributions into a ratio,<sup>5</sup>  $\Delta E_c:\Delta E_v = 85:15$ , was universally accepted; the results of several recent experiments,<sup>2</sup> however, have indicated a larger  $\Delta E_v \sim 0.45\text{--}0.55$  eV, and a ratio  $\Delta E_c:\Delta E_v \sim 60:40$ . Most of these results derive from extrapolation of the measurements at the  $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$  interface, with  $0.2 \leq x \leq 0.6$ .

Following Anderson's<sup>6</sup> early effort with an electron affinity rule, a few theoretical models<sup>1,7-11</sup> were proposed to calculate the valence-band offset at the interface of semiconductors. These models also fail to agree for the GaAs/AlAs interface: Harrison's<sup>7</sup> tight-binding approach gave too small a valence-band offset ( $\sim 0.04$  eV) [the difficulties of this approach with Al-containing compounds have been related<sup>8</sup> to the observed anomaly of the Al-X ( $X = \text{P}, \text{As}, \text{Sb}$ ) bond lengths entering this model]; Frenley and Kroemer<sup>9</sup> first found  $\Delta E_v = 0.26$  eV, and later, in a revised version,  $\Delta E_v = 0.69$  eV; the model recently proposed by Tersoff<sup>10</sup> gives  $\Delta E_v = 0.35$  eV; Van de Walle and Martin<sup>11</sup> constructed the model solid by superposing neutral atomic spheres to estimate  $\Delta E_v = 0.60$  eV. A common feature of all these theoretical approaches is that they evaluate the offset by the alignment of certain "reference levels" which are characteristic of the bulk semiconductors. In the same spirit, the absolute energy

positions of the deep-level impurities have been proposed<sup>12</sup> as reference energies; this yields  $\Delta E_v = 0.42$  eV. The empirical rule proposed by Bauer and Margaritondo<sup>1(a)</sup> and Katnani and Margaritondo<sup>1(b)</sup> gives 0.43 eV. The question has been raised if, indeed, the band offset can be determined by knowing only the properties of the separate bulk materials, i.e., without performing a calculation on the interface. The first published report of the AlAs/GaAs(110) valence-band offset based on a self-consistent study of the interface is the pioneering work of Pickett, Louie, and Cohen.<sup>13</sup> Using an empirical local-pseudopotential approach, they found  $\Delta E_v = 0.25$  eV, when the band offset is calculated by the relative alignment of the average potential on the two sides of the interface. Recently, the self-consistent *ab initio* non-local-pseudopotential method was applied by Van de Walle and Martin<sup>11</sup> to various heterojunctions; they obtained  $\Delta E_v = 0.37$  eV for AlAs/GaAs(110).<sup>11</sup>

In this Rapid Communication, we report a theoretical determination of the valence-band offset for the GaAs/AlAs interface based on the self-consistent all-electron energy-band-structure calculations for the  $(\text{GaAs})_n(\text{AlAs})_n(001)$  ( $n = 1, 2, 3$ ) superlattice. We use the core levels as reference energies to determine the relative alignment of the valence-band edges. We find a valence-band offset  $\Delta E_v = 0.5 \pm 0.05$  eV, in very good agreement with the recent experimental results. Since our determination of the band offset relies on quantities that are—in principle—experimentally accessible [e.g., by x-ray photoemission spectroscopy (XPS)<sup>3</sup>] a direct comparison with experiment is possible, which is different from the reference level used in the pseudopotential calculation.

Since GaAs and AlAs have almost the same lattice constant (the experimental mismatch is about 0.1%),<sup>14</sup> we used the same experimental value in all our calculations. The effect of strain,<sup>15</sup> which may be expected to be small for this closely matched heterojunction, is neglected in first approximation in this work. We have performed self-consistent full-potential linearized augmented-plane-wave (FLAPW)<sup>16</sup> calculations on the two bulk semicon-

ductors and on the  $(\text{GaAs})_n(\text{AlAs})_n(001)$  superlattices, with  $n \leq 3$ . The superlattices have a tetragonal structure (space group  $D_{2d}^1$ ), with lattice parameters  $a = a_0/\sqrt{2}$  and  $c = na_0$  and  $4n$  atoms per unit cell (and  $a_0$  is the zincblende lattice parameter).

Band energies were calculated semirelativistically, while the core states were treated fully relativistically and updated at each iteration. The Hedin-Lundqvist<sup>17</sup> form of the exchange-correlation potential was employed. The calculations on bulk GaAs and AlAs were performed by using ten special  $k$  points<sup>18</sup> in the irreducible wedge of the Brillouin zone, while for the  $n=2,3$  superlattices we used three special  $k$  points<sup>19</sup> in the two-dimensional- (2D-) like wedge of the Brillouin zone. (Calculations with more than three special  $k$  points showed that sufficient precision was obtained.) Inside the muffin-tin spheres, angular momenta up to  $l=8$  are used in the expansion of the wave functions, and up to  $l=4$  for the charge density and potential. In the interstitial regions, the wave functions are expanded in terms of all the plane waves with wave vector  $k \leq k_{\text{max}} = 2.48$  a.u. The resulting convergence, determined by the parameter  $k_{\text{max}}\langle R_{\text{MT}} \rangle \sim 5.7$ , where  $\langle R_{\text{MT}} \rangle$  is the average muffin-tin radius, is sufficient to lead to stable band eigenvalues and charge densities.

We have performed six independent self-consistent calculations in order to test the stability of the results with respect to the parameters entering the calculations. Particular attention was devoted to the treatment of the "semicore" Ga  $3d$  states. About 0.15 electrons spill out of each ( $R_{\text{MT}} = 2.3$  a.u.) muffin-tin sphere. Since the potential profile across the interface is very sensitive to the correct distribution of the electronic charge, we describe the spillout-core charge density by using the overlapping-charge method. A less precise treatment, such as the uniform spreading of this charge in the interstitial regions, results in an artificial charge transfer between the two sides of the interface and a remarkable alteration of the band lineup. This result indicates that the band lineup depends critically on the charge transfer at the interface. We have used different sets of sphere radii and also treated the Ga  $3d$  electrons as band states. The corresponding deviations in the  $\Delta E_v$  values are  $\sim 0.01$  and  $\sim 0.03$  eV, respectively. The remarkable consistency of these results provides evidence for the precision of our calculations.

Figure 1 shows a diagram of the energy levels near the interface. The binding energies of the selected core levels relative to the top of the valence bands ( $E_{c1}^b$  and  $E_{c2}^b$ ) are obtained from the self-consistent band structure of the bulk semiconductors. The superlattice calculation gives the binding-energy differences ( $\Delta E_B$ ) of the same core levels on the two sides of the interface, and finally,  $\Delta E_v$  is calculated from

$$\Delta E_v = E_{c1}^b - E_{c2}^b - \Delta E_B. \quad (1)$$

This approach assumes that in a heterostructure the binding energies of the core levels,  $E_{c1}^b$  and  $E_{c2}^b$  with respect to the corresponding valence-band maxima, are equal to their values in the bulk compounds when atoms are far enough away from the interface. However, since one deals with a finite-thickness superlattice in any model calculation, the concept of "local band structure," which was

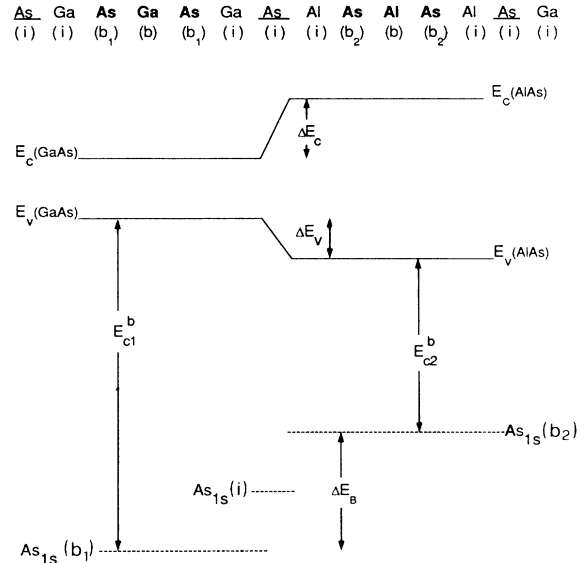


FIG. 1. Schematic diagram of the energy levels in the  $(\text{GaAs})_3(\text{AlAs})_3$  superlattice showing various quantities described in the text.

implicit in the previous assumption, is now lost. We therefore need to make the further assumption that in the superlattice the value of  $\Delta E_B$  is the same as in a real heterojunction. While the first assumption can be easily accepted, the second will be verified on the basis of our calculations.

To evaluate the band offset we have chosen the following representative core levels as the reference energies: As  $1s$ , As  $3d_{5/2}$  and Ga  $1s$ , Al  $1s$ . As seen from Fig. 1, in the  $(\text{GaAs})_3(\text{AlAs})_3$  superlattice two independent Ga (Al) sites exist, one (corresponding to two atoms) being "interface" [referred to as Ga( $i$ ) and Al( $i$ )] and the other being "bulk" [Ga( $b$ ) and Al( $b$ )]. On the other hand, three different As sites exist: (i) Two As atoms are on the GaAs side [As( $b_1$ )], (ii) two As atoms are on the AlAs side [As( $b_2$ )], and (iii) two As atoms are at the interface [As( $i$ )] and share two bonds with Ga( $i$ ) and two bonds with Al( $i$ ).

The core-binding-energy differences ( $E_{c1}^b - E_{c2}^b$ ) in the bulk compounds are given in Table I. A first remark on this data is related to the As core-level shifts in going from GaAs to AlAs: the change in binding energy of the As  $3d$  states ( $\sim 0.8$  eV larger in GaAs) is consistent with its slightly lower ionicity compared to AlAs.<sup>20,21</sup> A direct

TABLE I. Core-energy differences and corresponding valence-band offset values  $\Delta E_v$  in (i) the bulk compounds and (ii) the  $(\text{GaAs})_n(\text{AlAs})_n$  superlattices with  $n=2,3$ . Energies are in eV.

	$E_{c1}^b - E_{c2}^b$	$n=2$		$n=3$	
		$\Delta E_B$	$\Delta E_v$	$\Delta E_B$	$\Delta E_v$
As $1s$	0.87	0.44	0.43	0.41	0.46
As $3d_{5/2}$	0.81	0.37	0.44	0.34	0.47

comparison with x-ray photoemission spectroscopy experiments is also possible; Ludeke, Ley, and Ploog<sup>21</sup> found an upward shift in the As  $3d$  level of 0.6 eV going from GaAs to AlAs. The agreement of our result with their experiment (within the resolution of the measurement) supports the use of the local-density-approximation (LDA) core levels to calculate the valence-band offset.

Table I also lists the energy differences,  $\Delta E_B$ , of the chosen core levels on the two sides of the interface for the  $n=2,3$  superlattices, and the resulting  $\Delta E_v$  values. If we use the As  $1s$  and  $3d_{5/2}$  levels we get a valence-band offset  $\sim 0.47$  eV for the  $n=3$  superlattice and  $\Delta E_v \sim 0.44$  eV for the  $n=2$  case. This difference shows that an  $n=3$  superlattice is already thick enough to determine the band offset with good precision, and we can estimate the uncertainty due to the finite superlattice thickness to be of this magnitude. In this respect, a further test is provided by comparing the bulk and interface Ga (Al) core levels in  $(\text{GaAs})_3(\text{AlAs})_3$ . The Ga  $1s$  and Al  $1s$  core-energy difference is  $\sim 0.07$  eV smaller for the bulk than for the interface Ga (Al) atoms. If we use these levels and the bulk Ga and Al atoms, however, we get a larger (0.07 eV) value for the band offset than that calculated by using the As levels. This difference can be attributed to a nonperfect cancellation of errors when different core levels are used. [For instance, a smaller  $k_{\text{max}}=2.3$  cutoff gives different ( $\sim 0.04$  eV larger) Ga  $1s$ -Al  $1s$  energy separations, but very stable values for the As  $1s$  and As  $3d_{5/2}$  energy differences.]

In order to correctly compare these calculated results with experiment, we need to first consider the effect of spin-orbit coupling. Its effect on  $\Delta E_v$  can be expected to be small, since the top of the valence band is mainly As  $p$ -like in both GaAs and AlAs. We can now estimate the resulting corrections *a posteriori* using the known values of the spin-orbit splittings. The spin-orbit splitting  $\Delta_0$  shifts the top of valence bands by  $\frac{1}{3}\Delta_0$ , and we can therefore estimate the consequent change in  $\Delta E_v$  to be one-third of the difference between the spin-orbit splittings in GaAs and AlAs. Using published values<sup>22</sup> gives a positive increase  $=\frac{1}{3}(0.34-0.29)$  eV  $\sim 0.02$  eV toward a larger offset. In the *worst* (highly conservative) case of adding this uncertainty to our earlier uncertainty from the difference between the  $n=2$  and 3 results, our valence-band offset is 0.5 eV with an uncertainty  $\leq 0.05$  eV. Thus our result appears to be in very good agreement with the latest experimental results,<sup>2</sup> which give  $\Delta E_v \sim 0.45$ -0.55 eV.

The fact that the offset is already established after only a very few layers is consistent with the results of Pickett *et al.*<sup>13</sup> for the (110) GaAs/AlAs interface and of Van de Walle and Martin<sup>15</sup> for the Si/Ge interface. To further verify this conclusion, we have calculated the angular-momentum-decomposed charges  $Q_l$  inside the muffin-tin spheres; their values in the superlattice are compared with those in the bulk in Table II. The results show that (i) the  $Q_l$  values in the  $n=3$  superlattice are very similar to those of the bulk compounds, and (ii) the two adjacent Ga (Al) atoms have (within our numerical precision) exactly the same  $Q_l$  values. Further, in order to prevent any numerical difference (such as different structure of  $k$ -point

TABLE II.  $l$  decomposition of the charge density inside muffin-tin spheres (radii are 2.3 a.u.).

	$Q_s$	$Q_p$	$Q_d$	$Q_{\text{tot}}$
GaAs (bulk)				
Ga	0.84	0.74	0.09	1.69
As	1.35	1.88	0.04	3.28
AlAs (bulk)				
Al	0.64	0.68	0.10	1.44
As	1.35	2.01	0.03	3.40
$(\text{GaAs})_3(\text{AlAs})_3$				
Ga( <i>b</i> )	0.84	0.73	0.09	1.68
Ga( <i>i</i> )	0.84	0.73	0.09	1.68
Al( <i>i</i> )	0.65	0.66	0.10	1.43
Al( <i>b</i> )	0.65	0.66	0.10	1.43
As( <i>b</i> <sub>1</sub> )	1.36	1.87	0.04	3.27
As( <i>i</i> )	1.35	1.94	0.04	3.33
As( <i>b</i> <sub>2</sub> )	1.35	2.00	0.03	3.39

meshes) from affecting our conclusions, we performed self-consistent calculations on the  $n=1$  superlattice, and on the two bulk compounds in the  $n=1$  superlattice structure,  $D_{1d}^1$ . The  $l$ -decomposed integrated charge differences inside the Ga and Al muffin-tin spheres are smaller than 0.8%, while the As  $Q_l$  value is halfway be-

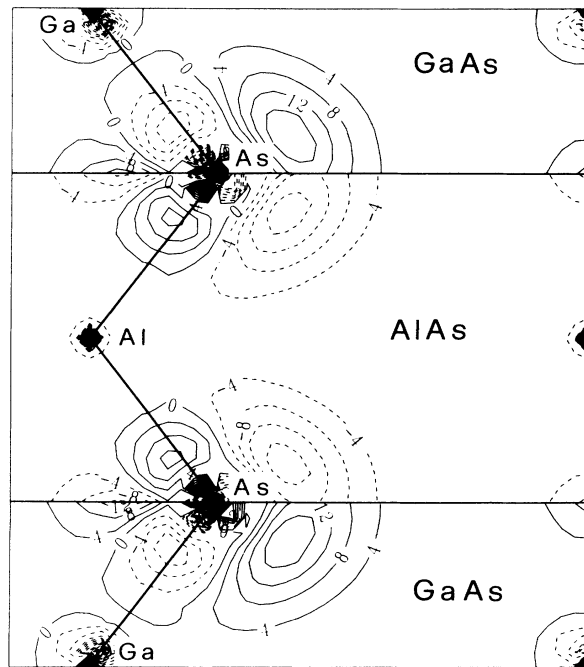


FIG. 2. Difference between the charge density of  $(\text{GaAs})_1(\text{AlAs})_1$  and those of the bulk semiconductors. Contours are given in units of  $10^{-4}e/a_0^3$ , i.e.,  $\sim 0.06$  electrons per unit cell.

tween the GaAs and AlAs bulk values. In order to demonstrate the interface effects, we show in Fig. 2 contour plots of the difference between the charge density of the  $(\text{GaAs})_1(\text{AlAs})_1$  superlattice and those of the pure compounds. These charge-density deformations, which give rise to the induced interface dipole moment at an abrupt interface, are seen to be quite small (note the scale in Fig. 2), and to fall off very rapidly away from the As interface atom. Surprisingly, we recover almost bulklike properties already in the first Ga and Al atoms away from the interface.

Finally, a question concerning the validity of our results could arise from the use of the local-density approximation. However, since we only use the LDA to derive the valence-band discontinuity, the well-known band-gap problem should not affect our results. Furthermore, although the energies of localized states such as the core states are usually poorly described by the LDA, we believe that relative energy differences are meaningful. In this context, let us look at the XPS measurements. Waldrop *et al.*<sup>23</sup> reported  $\Delta E_v \sim 0.4$  eV for GaAs grown on AlAs(110) and  $\Delta E_v \sim 0.15$  eV for the reverse sequence,

which raised the question of the commutativity of the offset. More recent XPS measurements,<sup>3</sup> however, gave a commutative  $\Delta E_v = 0.38\text{--}0.39$  eV. Unfortunately, the absolute value of the offset in these experiments relies on an accurate knowledge of the binding energies of the core levels in the bulk semiconductors; a precise value of the Al  $2p$  binding energy is, however, lacking.<sup>3</sup> Thus, comparison between our results and experiment (while agreeing within the uncertainty of the experiment) requires a more precise measurement of the core binding energy.<sup>1,3</sup>

In conclusion, using the first-principles FLAPW band-structure method, we have obtained the valence-band offset for the GaAs/AlAs interface. Using the core levels as reference energies produces a very good value compared to experiment and may turn out to be an important tool for predicting the band offset of semiconductor heterojunctions.

This work was supported by the National Science Foundation through the Northwestern University Materials Research Center Grant No. DMR 852028.

\*Present address: Argonne National Laboratory, Argonne, IL 60439.

<sup>1</sup>(a) R. S. Bauer and G. Margaritondo, *Phys. Today* **40** (No. 1), 27 (1987), and references therein; (b) A. D. Katnani and G. Margaritondo, *Phys. Rev. B* **28**, 1944 (1983).

<sup>2</sup>For recent critical reviews, see H. Kroemer, *J. Vac. Sci. Technol. B* **2**, 433 (1984); G. Duggan, *ibid.* **3**, 1224 (1985). The most recent results, to our knowledge, are reported in A. D. Katnani and R. S. Bauer, *Phys. Rev. B* **33**, 1106 (1986); B. A. Wilson, P. Dawson, C. W. Tu, and R. C. Miller, in *Layered Structures and Epitaxy*, Materials Research Symposium Proceedings, Vol. 56, edited by J. M. Gibson, G. S. Osbourn, and R. M. Tromp (Materials Research Society, Pittsburgh, PA, 1986), p. 307; *Appl. Phys. Lett.* **48**, 541 (1986); J. Batey and S. L. Wright, *J. Appl. Phys.* **59**, 200 (1985).

<sup>3</sup>Katnani and Bauer, Ref. 2.

<sup>4</sup>Wilson *et al.* and Batey and Wright, Ref. 2.

<sup>5</sup>R. Dingle, W. Wiegmann, and C. H. Henry, *Phys. Rev. Lett.* **33**, 827 (1974).

<sup>6</sup>R. L. Anderson, *Solid State Electron.* **5**, 341 (1962); see also, C. Mailhot and C. B. Duke, *Phys. Rev. B* **33**, 1118 (1986); J. L. Freeouf and J. M. Woodall, *Surf. Sci.* **168**, 518 (1986).

<sup>7</sup>W. A. Harrison, *J. Vac. Sci. Technol.* **14**, 1016 (1977). Recently, W. A. Harrison and J. Tersoff [*J. Vac. Sci. Technol. B* **4**, 1068 (1986)] reported  $\Delta E_v = 0.12$  eV, including the effect of screening. See also P. Vogl, H. P. Hjalmarson, and J. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983).

<sup>8</sup>S. Gonda, *Solid State Commun.* **60**, 249 (1986).

<sup>9</sup>W. R. Frensley and H. Kroemer, *J. Vac. Sci. Technol.* **13**, 810 (1976); *Phys. Rev. B* **16**, 2642 (1977).

<sup>10</sup>J. Tersoff, *Phys. Rev. B* **30**, 4874 (1984); *Phys. Rev. Lett.* **56**, 2755 (1986).

<sup>11</sup>C. G. Van de Walle and R. M. Martin, *J. Vac. Sci. Technol. B* **4**, 1055 (1986).

<sup>12</sup>J. M. Langer and H. Heinrich, *Phys. Rev. Lett.* **55**, 1414 (1985); M. J. Caldas, A. Fazzio, and A. Zunger, *Appl. Phys. Lett.* **45**, 671 (1984).

<sup>13</sup>W. E. Pickett, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **17**, 815 (1978); see also a recent calculation by A. C. Ferraz and G. P. Srivastava, *Semicond. Sci. Technol.* **1**, 169 (1986).

<sup>14</sup>*Handbook of Chemistry and Physics*, edited by R. W. Weast (Chemical Rubber Company, Boca Raton, FL, 1985).

<sup>15</sup>C. G. Van de Walle and R. M. Martin, *Phys. Rev. B* **34**, 5621 (1986).

<sup>16</sup>H. J. F. Jansen and A. J. Freeman, *Phys. Rev. B* **30**, 561 (1984).

<sup>17</sup>L. Hedin and B. I. Lundqvist, *J. Phys. C* **4**, 2064 (1971).

<sup>18</sup>D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).

<sup>19</sup>S. L. Cunningham, *Phys. Rev. B* **10**, 4988 (1974).

<sup>20</sup>J. Ihm and J. D. Joannopoulos, *Phys. Rev.* **24**, 4191 (1981).

<sup>21</sup>R. Ludeke, L. Ley, and K. Ploog, *Solid State Commun.* **28**, 57 (1978).

<sup>22</sup>J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), cf. Table 7.3.

<sup>23</sup>J. R. Waldrop *et al.*, *J. Vac. Sci. Technol.* **19**, 573 (1981).