Surface Science at Atmospheric Pressure: Reconstructions on (001) GaAs in Organometallic Chemical Vapor Deposition

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We report the first observation of reconstructions on semiconductor surfaces in atmospheric pressure (AP) environments. Using reflectance-difference spectroscopy we show that the primary reconstructions that occur on (001) GaAs in ultrahigh vacuum (UHV) also occur under AP H_2, He, and N_2. These results demonstrate that dimer formation is not restricted to surfaces in UHV and justify the use of UHV studies to determine (001) GaAs chemistry during AP organometallic chemical vapor deposition (OMCVD). Reconstructions observed during OMCVD growth are inconsistent with previous models and provide new insights concerning growth.

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Reconstructions on (001) GaAs in ultrahigh vacuum (UHV) have been studied extensively by reflection high-energy electron diffraction (RHEED) [1,2], low-energy electron diffraction (LEED), [3] x-ray diffraction (XRD) [4], and scanning tunneling microscopy (STM) [5], typically on surfaces prepared by molecular-beam epitaxy (MBE). The primary reconstructions that are stable over reasonable ranges of conditions include those with (4×2), (2×4), and $c(4\times4)$ long-range order (LRO). It is presently accepted that these surfaces are terminated by Ga dimers along [110], As dimers along [$\bar{1}$10], and As dimers along [110], respectively, where every fourth dimer is missing to achieve local charge neutrality [6]. In contrast, due to the lack of appropriate surface analytical techniques little is known about surfaces under atmospheric pressure (AP) or near-AP conditions, such as those that determine reaction pathways during organometallic chemical vapor deposition (OMCVD). Because surfaces in UHV are usually very reactive, it has been speculated that (001) GaAs surfaces under AP would be quite different from surfaces in UHV, for example, terminated by hydrogen in OMCVD [7,8].

Here, we use reflectance-difference spectroscopy (RDS), a surface-sensitive optical probe, to bridge the gap between the well-characterized (001) GaAs surfaces prepared in UHV by MBE and the previously uncharacterized (001) GaAs surfaces prepared in AP H_2, He, and N_2 by OMCVD. Our data show that (001) GaAs also reconstructs under AP H_2, He, and N_2 to form both Ga and As dimers, yielding surface terminations that are locally virtually identical to those that occur in UHV. For equivalent substrate temperatures and As fluxes we observe all primary reconstructions, (4×2), (2×4), $c(4\times4)$, and a high-As-coverage disordered structure that we recently reported [9] and termed $d(4\times4)$, in both UHV and AP. Our data reveal from several perspectives that (001) (GaAs) surfaces during MBE and OMCVD growth have many similarities, differing primarily in equilibrium coverages of As.

Experiments were performed with a Varian Gen II MBE station and a double-wall horizontal-flow OMCVD reactor. After standard chemical treatments, samples were mounted on a Mo sample block in the MBE station and on a SiC-coated graphite susceptor in the OMCVD reactor. To eliminate possible complications from the linear electro-optic effect [10] we used semi-insulating substrates or grew undoped buffer layers. Details of RDS [11] and the method by which effects of strain birefringence in the transparent quartz walls of the OMCVD reactor were compensated are described elsewhere [9]. Briefly, RDS determines $\Delta\tilde{r}/\tilde{r}=(\tilde{r}_{\bar{1}10}-\tilde{r}_{110})/\tilde{r}=\Delta r/r+i\Delta\theta$, where $\tilde{r}_{\bar{1}10}$ and $\tilde{r}_{110}$ are the complex reflectances of light linearly polarized along [$\bar{1}$10] and [110], respectively. Since cubic semiconductors are nominally optically isotropic, the ordinarily dominant (>99%) bulk contribution to the reflectance essentially cancels in subtraction, leaving that from the lower-symmetry surface. With compensation $\Delta r/r$ can be obtained essentially free of experimental artifacts, so we use this quantity throughout.

Typical RD spectra for the primary reconstructions on (001) GaAs in various ambients are summarized in Figs. 1 and 2. We consider first the results on surfaces in UHV, which were simultaneously characterized by RHEED and form the database for analysis of surfaces under AP.

The major features of these spectra originate from electronic transitions between energy levels of the local atomic structures and can be uniquely related to specific surface dimers [12]. The negative 1.9-eV feature of the (4×2) spectrum is due to transitions between bonding Ga dimer orbitals and empty Ga lone-pair states, while the positive 2.6- and 4.2-eV features of the (2×4) spectra are due to transitions between As lone-pair and empty As antibonding dimer levels and between bonding and antibonding As dimer orbitals, respectively. The 2.6-eV feature of the $c(4\times4)$ spectrum [13] is inverted relative to (2×4) because the orientation of the As dimers differs

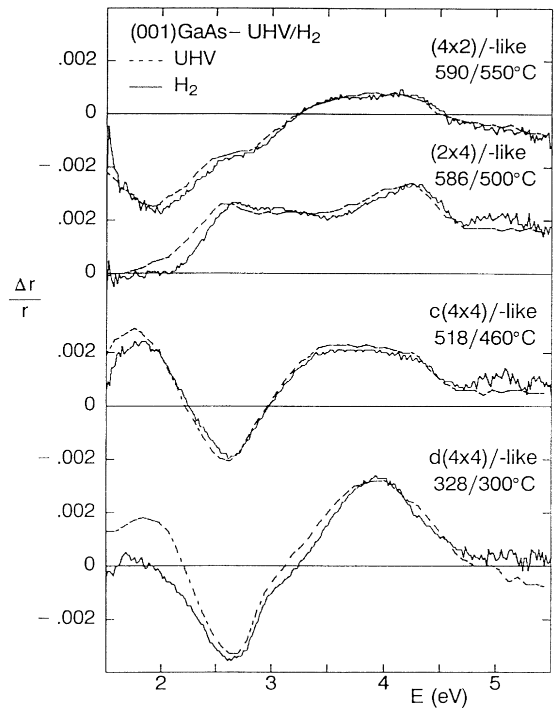

FIG. 1. RD spectra of the primary reconstructions on (001) GaAs in UHV and AP H_2. Sample temperatures for the UHV/H_2 ambients are indicated. The surfaces in UHV were prepared under an As_4 beam equivalent pressure (BEP) of 5×10^{-9} Torr for the (4×2) reconstruction and 5.7×10^{-5} Torr for the rest. The BEP is the reading of the ionization gauge when it is placed at the substrate location.

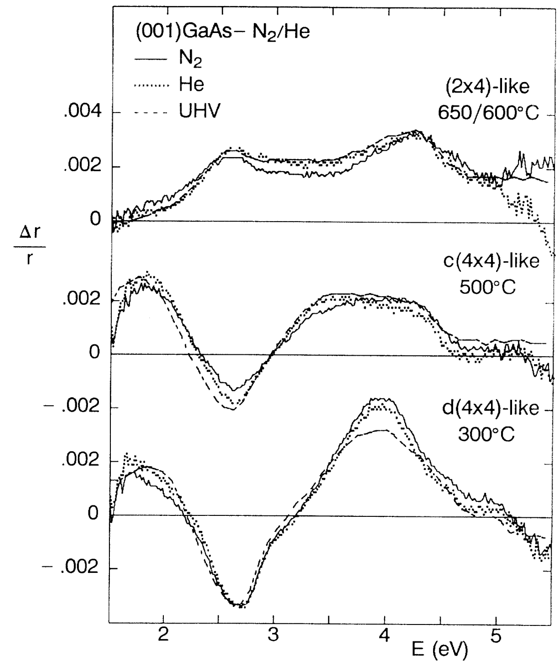

FIG. 2. As Fig. 1, but for ambients of He and N_2. The UHV data are the same as those of Fig. 1.

by 90° in the two cases. The $d(4\times4)$ reconstruction is formed by adding excess As to $c(4\times4)$ and is distinguished in RDS by a peak at 4.0 eV and in RHEED by weakened half-order streaks.

We now consider the results for AP ambients. Samples were prepared under a constant flow of AP H_2, He, or N_2, with AsH_3 and triethylgallium introduced as necessary. The H_2 data are compared directly with the UHV results in Fig. 1; the analogous comparison for He and N_2 is given in Fig. 2. The conclusion is obvious and striking: Under equivalent static conditions, the same RD spectra can be obtained regardless of whether the (001) GaAs surface is in UHV, or under H_2, He, or N_2. Since these spectra originate from specific local atomic structures, we conclude that the surface terminations that give rise to similar RD spectra are themselves locally identical, possibly even identical with respect to LRO. Thus dimer formation is not restricted to surfaces in UHV, but may be a quite general phenomenon. We term AP reconstructions "-like" because the optical data originate from local atomic structure instead of the LRO from which the original (4×2), (2×4), and $c(4\times4)$ nomenclature derives. However, under static conditions we expect LRO to form, as shown by a recent XRD study performed under 100 Torr H_2 [14]. But we also note that the significant property for surface reactions is the local atomic structure, not LRO.

Further evidence of the similarity of (001) GaAs surfaces in UHV and under AP H_2 is provided in Fig. 3, which shows the (2×4)-$c(4\times4)/d(4\times4)$ phase diagram obtained from data taken at different sample temperatures over nearly 10 orders of magnitude of the As incorporation rate [15]. The As-containing precursor was As_4 for the UHV data shown at the bottom and AsH_3 for the AP H_2 data at the top, although the actual species reacting with the surface under AP H_2 was probably As_2 or As_4 as a result of pyrolytic or heterogeneous cracking of AsH_3 [16]. The solid circles, crosses, and open circles represent (2×4), $c(4\times4)/d(4\times4)$, and mixed structures, respectively. The solid line is the (2×4)-$c(4\times4)$ boundary established by Van Hove, Cohen, and Lent in UHV [2] and the dashed lines are its extrapolations. We note that this single straight line separates the (2×4) and $c(4\times4)$ regions over nearly 10 orders of magnitude, further indicating that the only essential difference between these surfaces is the shift of the equilibrium point due to the vastly higher partial pressures of As-containing species that are typical of AP environments. This similarity between (001) GaAs surfaces in UHV and AP can be used to justify the applicability of UHV studies [17] of (001) GaAs chemistry to AP OMCVD growth.

The (4×2) surface is highly reactive, as shown by the difficulty of preparing the pure phase under AP H_2 and its tendency to be readily contaminated by even minute

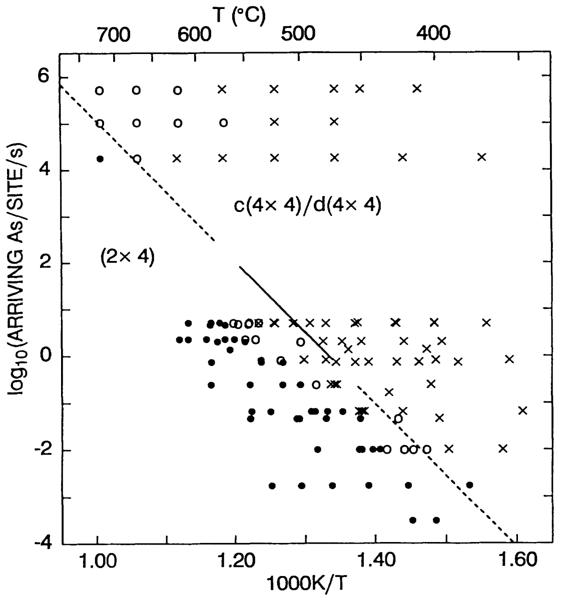

FIG. 3. (2×4)-c(4×4)/d(4×4) phase diagram of (001) GaAs as a function of substrate temperature and incorporation rate of As atoms, determined as described in [15]. Solid circles, crosses, and open circles represent (2×4)-like, c(4×4)/d(4×4)-like, and mixed structures, respectively, as established by RDS. The solid line shows the (2×4)/c(4×4) phase boundary obtained by Van Hove, Cohen, and Lent (Ref. [2]).

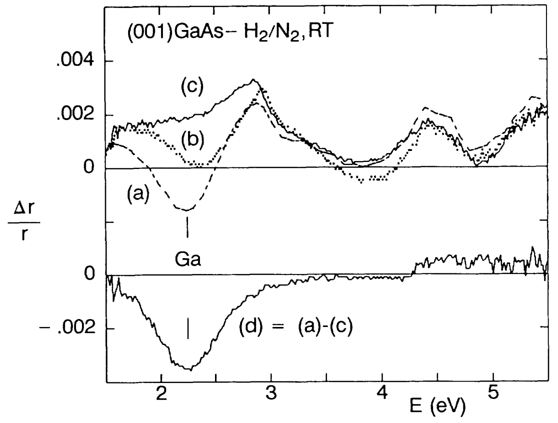

FIG. 4. RD spectra obtained from surfaces in OMCVD trace: a, after cooling the (4×2)-like surface prepared at 550 °C in H_2 to RT; b, 50 min after replacing H_2 with N_2; c, after annealing b at 300 °C for 6 min, then cooling to RT; and d, the difference $a - c$.

background amounts of As. In contrast, As-terminated surfaces are relatively stable. We took advantage of these properties to isolate the Ga dimer contribution to RDS spectra by preparing a (4×2)-like surface at 550 °C in AP H_2, cooling it to room temperature (RT), then exposing it to N_2 or He. During cooling the surface evolved to a mixture of Ga and As terminations as shown in Fig. 4, trace a. When this surface was exposed to N_2, the spectrum evolved to that shown as b, and after annealing at 300 °C for 6 min, to that shown as c. By subtracting trace a from b or c, we find no change at 2.9 and 4.5 eV, the energies of the As features at RT; hence we assign the change at 2.2 eV to Ga dimers. The narrow feature in d is the first clear picture of the isolated Ga dimer contribution. We believe that this change is due to the reaction of Ga dimers with N_2 or impurities. The same result was obtained with He. These results are relevant to the XRD data of Fuoss *et al.*, which indicated no reconstructions on (001) GaAs under 100 Torr N_2 [14]. We attribute this absence of LRO to surface disorder induced by adsorption at Ga sites. We did not prepare (4×2)-like surfaces in N_2 and He for practical reasons, but the Ga reactivity will make their formation in these ambients difficult.

Because a given LRO can exist for a range of surface stoichiometries, the RD spectra of some reconstructions depend noticeably on substrate temperature and As flux. The (2×4) spectrum is relatively invariant over a wide range of conditions because the potential barrier for As desorption is high. For c(4×4) and d(4×4) the As coverage is determined more directly by competition between adsorption and desorption, and also by diffusion and ordering. The c(4×4) reconstruction exists over a narrower range of conditions than d(4×4). These results suggest the presence of at least three distinct bonding configurations for As. This is consistent with recent observations by Creighton and Banse [18], who performed temperature-stimulated desorption measurements of excess As deposited by AsH_3 on Ga-rich (001) GaAs at 275 °C and also found three states of As at the surface. They assigned the 570 °C desorption peaks to (2×4) As based on LEED observations. We would assign their 490 and 420 °C desorption peaks to c(4×4) and d(4×4), respectively.

Our results show that the most significant difference between (001) GaAs surfaces during OMCVD and MBE growth is the presence of two or more layers of As on the surface during OMCVD. We see no evidence of the formation of stable Ga dimers at any stage during growth by atomic layer epitaxy. No previous model of OMCVD growth has considered either possibility. Therefore, our results provide new insights for understanding fundamental processes of growth. For example the absence of Ga dimers explains why high-quality material can be prepared by OMCVD; the As-stabilized surface is relatively inert and thus not susceptible to impurity contamination.

Other implications also follow. The quality of fractional-layer superlattices is higher with the substrate misoriented toward [$\bar{1}$10] for OMCVD [19] and [110] for MBE [20]. The discrepancy was attributed to the lack of dimer formation in OMCVD [7], but our results show that this cannot be the case. Instead, the difference in dimer orientations on these surfaces under their respective As-stabilized conditions may be responsible, possibly through anisotropic diffusion. Finally, for several theories of self-ordering in ternary III-V semiconductor alloys [21] the existence of surface dimers in OMCVD is crucial. While our work does not prove their existence for InP-based materials, the observation of dimers on one III-V alloy provides clear support for this model.

In conclusion, we have observed the formation of As and Ga dimers on (001) GaAs under atmospheric pressure ambients using reflectance-difference spectroscopy. Our results not only provide information on the mechanisms of OMCVD of GaAs, but also suggest new opportunities for surface science in general.

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