Scanning Microscopy

Volume 8 | Number 4 Article 14

12-13-1994

ZnSe Heteroepitaxial Growth on Si (100) and GaAs (100)

D. K. Biegelsen
Xerox Palo Alto Research Center, biegelsen@parc.xerox.com

R. D. Bringans
Xerox Palo Alto Research Center

J. E. Northrup
Xerox Palo Alto Research Center

L. -E. Swartz
Xerox Palo Alto Research Center

Recommended Citation

Biegelsen, D. K.; Bringans, R. D.; Northrup, J. E.; and Swartz, L. -E. (1994) "ZnSe Heteroepitaxial Growth on Si (100) and GaAs (100)," *Scanning Microscopy*: Vol. 8 : No. 4 , Article 14.
Available at: https://digitalcommons.usu.edu/microscopy/vol8/iss4/14

Scanning Microscopy, Vol. 8, No. 4, 1994 (Pages 883-888) 0891-7035/94$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

ZnSe HETEROEPITAXIAL GROWTH ON Si (100) AND GaAs (100)

D.K. Biegelsen*, R.D. Bringans, J.E. Northrup and L.-E. Swartz

Xerox Palo Alto Research Center, Palo Alto, CA 94304

(Received for publication June 23, 1994 and in revised form December 13, 1994)

Abstract

The early stages of ZnSe heteroepitaxy on Si(100), Si(100):As and GaAs(100) are compared and contrasted, based on results of scanning tunneling microscopy and photoemission spectroscopy. High Se reactivity with the substrate constituents leads to bulk phase formation which is detrimental to heteroepitaxy. As-termination of Si(100) not only passivates the surface, but also provides an ideal buffer for ZnSe overgrowth. Lacking a similar buffer layer, stoichiometric control of the GaAs(100) surface is investigated to find a means for controlled heteroepitaxy.

Key Words: Heteroepitaxy, As-termination, zinc selenide, gallium arsenide, silicon.

*Address for correspondence and present address:
David K. Biegelsen
Xerox Palo Alto Research Center,
3333 Coyote Hill Road,
Palo Alto, CA 94304
Telephone number: (415) 812-4137
FAX number: (415) 812-4140
E-mail: biegelsen@parc.xerox.com

Introduction

Controlled heteroepitaxial film growth requires that the overlayer proceed through a progression of effectively two dimensional structures. The structures are generally metastable. Competing configurations having lower energy must be, if possible, kinetically constrained. The growth of ZnSe on Si and GaAs presents interesting examples where the chemical configurations can, in principle, be energetically stable at each stage. The crystal grower might then be aligned with nature in achieving the desired goal. In this paper, we contrast the early stages of film evolution for ZnSe on Si(100) and GaAs(100).

Results and Discussion

The ideally terminated Si(100) surface has two singly occupied dangling bonds per surface atom. Dimerization lowers the total energy but leaves the surface highly reactive. One monolayer (ML) of two-fold coordinated Se bridging between Si atoms results in a relatively low energy structure (Bringans and Olmstead, 1989) and might be expected to form a passivating layer.

In previous work (Bringans *et al.*, 1992), it has been shown that ZnSe deposition directly on Si at elevated temperatures results in polycrystalline overgrowth. The reason is that the heat of formation of $SiSe_2$ is strongly negative. This driving force coupled with the low average coordination of $SiSe_2$ leads to a diffusion-limited growth of bulk, glassy $SiSe_2$ at moderate temperatures. Thus, even in the presence of Zn, the Se ambient converts the Si from an epitaxial template to a noncrystalline substrate. The kinetic barrier separating the metastable Se-monolayer termination from the much lower-energy bulk $SiSe_2$ is too low to be useful. Depositing Zn first (Park and Mar, 1986) or using very low substrate temperatures (Bringans *et al.*, 1992) reduces the reaction but also produces poor epitaxial growth.

Arsenic termination of Si(100) has also been shown to be energetically very favorable (Uhrberg *et al.*, 1986). Furthermore, there is a high kinetic barrier to Si_xAs_y formation. Most importantly, though, for its use

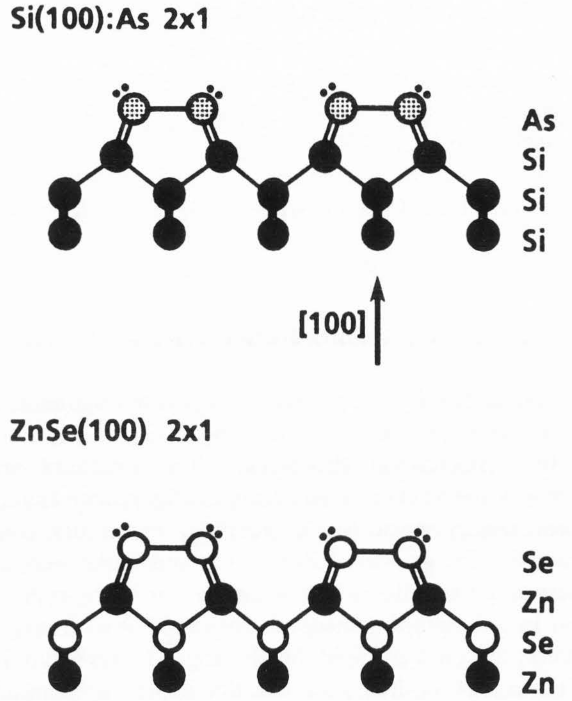

Figure 1. Ball and stick models of (top) As on Si(100) and (bottom) ZnSe on GaAs(100). The structures are projected along the [011] direction.

as a template for ZnSe heteroepitaxy, the Si(100):As 2x1 dimerized surface, shown schematically in Figure 1 (top), is isoelectronic and structurally equivalent to the Se terminated ZnSe(100) 2x1 surface [Fig. 1 (bottom)]. In both cases, the surface atoms have three electrons per atom available for epitaxial overgrowth. From an incident Zn atom perspective, the Si(100):As surface looks like a Se-terminated bulk ZnSe(100) surface. Although the dimerized As atoms on Si(100) are fully coordinated, the dimer bond can be broken, leaving fewer than two electrons per orbital to contribute to subsequent covalent bonds. It was, therefore, expected (D.J. Chadi, personal communication) and shown experimentally (Bringans *et al.*, 1992) that ZnSe heteroepitaxy on Si(100):As is analogous to growth of chemically similar but lattice mismatched epitaxy, such as ZnSe on ZnS. (Note that one significant difference is that, unlike for polar semiconductor (100) surfaces, single atom height steps can be prevalent on group IV surfaces and can lead to antiphase domains in the II-VI overlayer.) Figure 2 shows the uniform epitaxial growth of a thin overlayer of ZnSe on Si(100):As (Bringans *et al.*, 1992). Using energy dispersive X-ray spectroscopy in the transmission electron microscope (TEM), the As monolayer has been shown (Romano *et al.*, 1994) to be pinned to the interface even after annealing to 900°C. Thus, the initial and final stages of growth of Si(100):As/ZnSe are energetically stable. The As monolayer is both a surface and interface passivant. [It is instructive to note that this is not the case for the (111) interface. Here also all Si dangling bonds are replaced by doubly occupied, low energy, As lone pairs. All atoms are again fully coordinated. However, with no dimer bonds to open, all surface orbitals are doubly occupied and only dative bonding can occur with any adsorbed species. In the alternative but equivalent view, there is no analogous, isoelectronic surface of ZnSe(111) which can satisfy the electron counting criteria. Therefore, the As ML does not support heteroepitaxy on the (111) surface and the As is a surface passivant only.)

We now turn to the evolution of ZnSe growth on GaAs(100). Here again, there is a strong thermodynamic driving force (high negative enthalpy) for compound formation (e.g., GaSe, Ga_2Se_3 and As_2Se_3; Li and Pashley, 1994). Another similarity to the growth on Si is the existence of a stable termination of the substrate which should also be energetically favorable as an interface. Harrison *et al.* (1978) first pointed out that electron counting arguments leading to covalent bond saturation and interface neutrality usually represent the dominant energetic term. They further showed that a simple, low energy interface arrangement between binary compound semiconductors arises from a 50:50 mixture of respective cations or anions. Charge transfer between nearby compensating, over- and under-coordinated pairs leads to interface neutrality and dipole minimization. For the case of ZnSe coverage of GaAs (100), Farrell *et al.* (1988) have proposed, and Figure 3a shows, a possible configuration where a half monolayer of As-Zn bonds (electron deficient) is compensated by a half monolayer of Se-Ga (electron-rich) bonds. A related possibility, having cation mixing, is shown in Figure 3b.

It is now becoming accepted that the dominant GaAs (100) surface reconstruction existing under the usual As-rich growth conditions in molecular beam epitaxy (MBE) is a 2x4 structure consisting of two As-As dimers (Biegelsen *et al.*, 1990; Bressler-Hill *et al.*, 1992; Hashizume *et al.*, 1994) atop a complete Ga layer ["α (2x4) phase"] or over a 3/4 ML Ga layer ["β2(2x4) phase"] as shown in Figures 4a and 4b, respectively. The former would be ideal for the anion-mixed interface. Similarly, a β2(4x2) phase consisting of two Ga-Ga dimers atop a complete As monolayer (Fig. 4c) would, in principle, be ideal for the inverted ZnSe overgrowth as shown in Figure 3b.

Unfortunately, for control of crystal growth, the energetics deflect the pathway of film evolution away from the ideal. Although, scanning tunneling microscopy (STM) shows highly ordered dimerization of the Se-reacted GaAs (100) surface (see Figs. 5a and 5b),

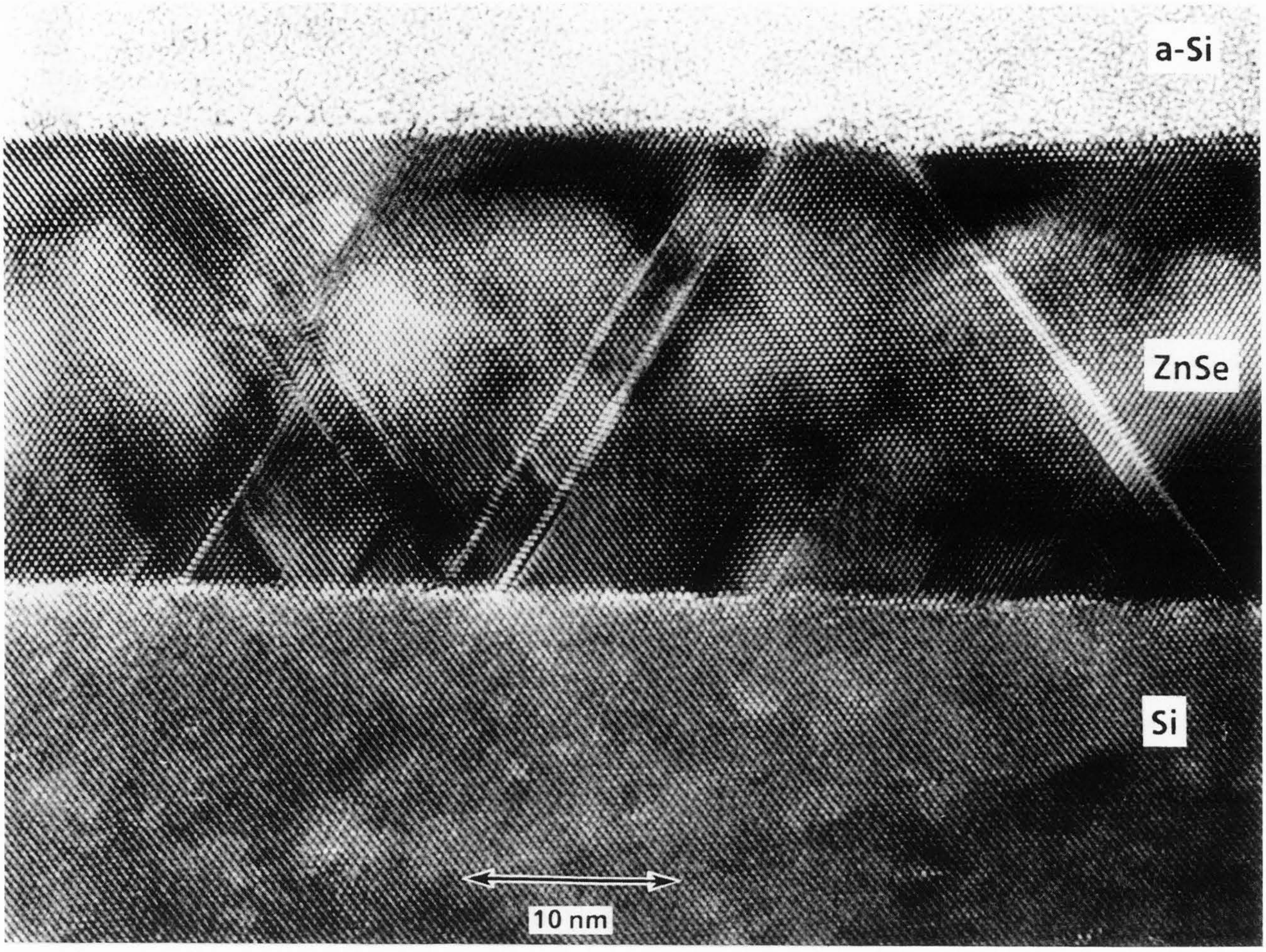

Figure 2. TEM cross-section of ZnSe grown on Si(100):As showing the abrupt interface and uniform overgrowth (capping layer of $\alpha-$Si is added during TEM sample preparation). (Reprinted from Bringans *et al.*, 1992)

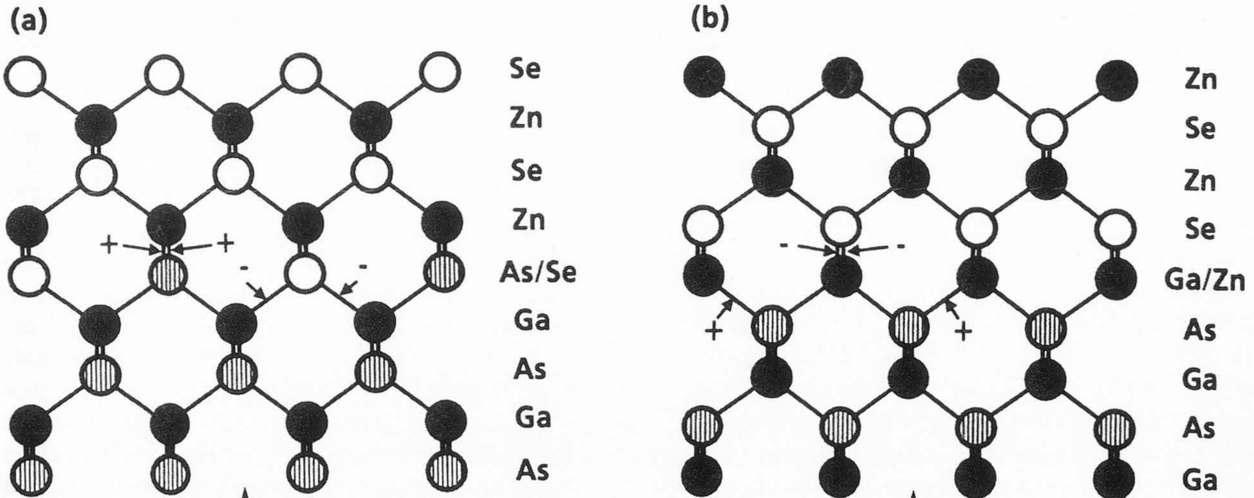

Figure 3. Ball and stick models of ZnSe/GaAs(100) interfaces with intermixed (**a**) anion or (**b**) cation layers. The minus (plus) signs indicate excess (deficient) electron concentration.

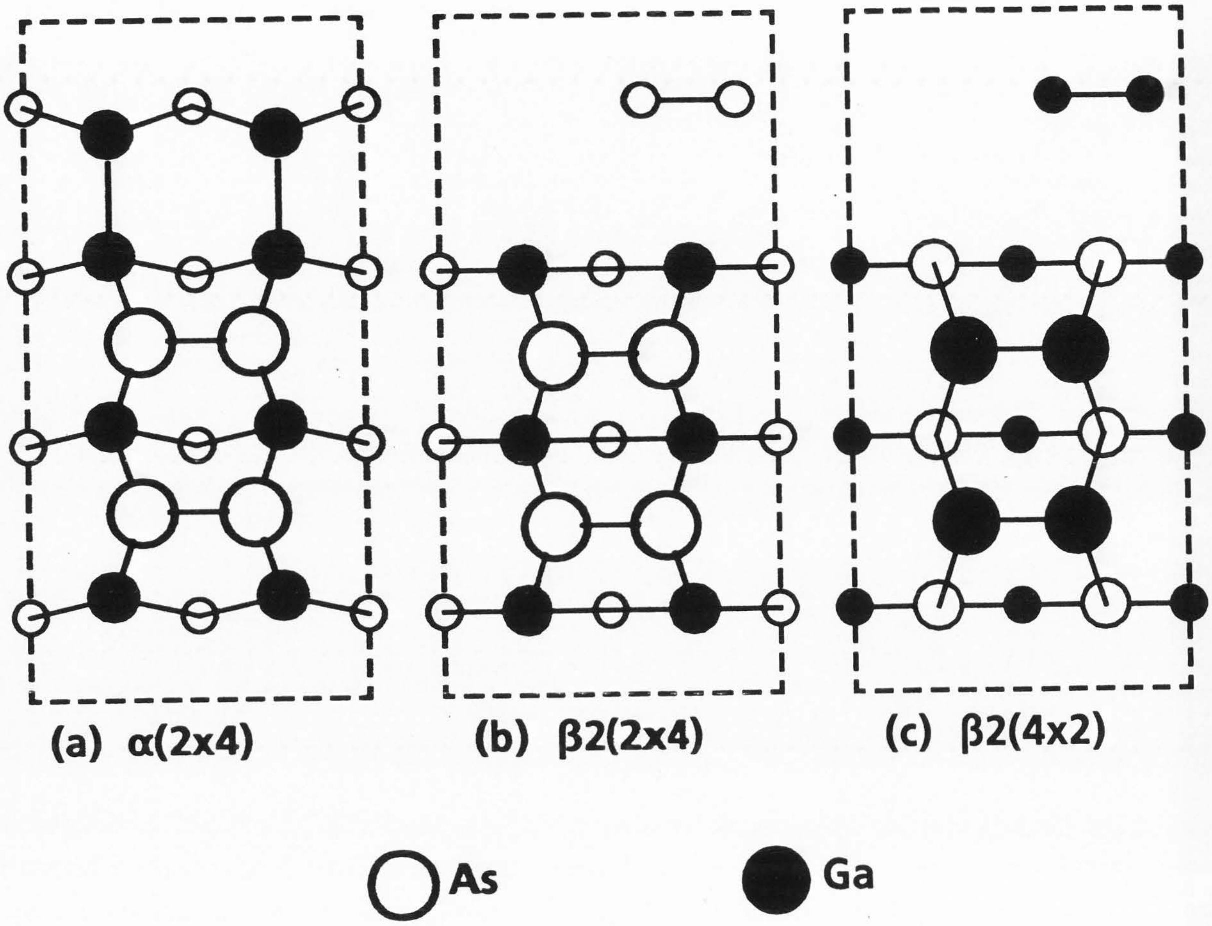

Figure 4. Ball and stick models of GaAs(100) 2x4 and 4x2 reconstructions; (a) α(2x4), (b) β2(2x4), and (c) β2(4x2), respectively. The [011] direction is parallel to the vertical axis in (a) and (b) and parallel to the horizontal axis in (c). (Reprinted from Northrup and Froyen, 1994)

concurrent X−ray photoemission spectroscopy measurements show that the surface is not simply terminated by a 50:50 mixture of Se and As (Biegelsen *et al.*, 1994). An initial uptake of approximately one Se ML occurs, exchanging with 1 ML of As, followed by a slowly increasing exchange of Se for As and a concomitant loss of Ga (Biegelsen *et al.*, 1994; Chambers and Sundaram, 1991; Takatani *et al.*, 1992). The STM images in Figure 5 were taken on samples prepared using a Se fluence equivalent to 4 nm thickness of bulk Se. The near−surface stoichiometry has been shown to be changing very slowly with fluence in this regime and STM images are independent of the particular fluence. This surface should therefore be representative of the ion−exchanged surface generally found under similar conditions. It has not been possible to determine if the dimers are Se−Se, Se−As or other. In any case, a bulk reaction occurs in the Se−rich regime which undermines the creation of an ideal anion−mixed interface overlying ideal bulk GaAs. Li and Pashley (1994) have inferred from their STM results that the Se surface reaction directly leads to the 3d overgrowth of ZnSe. Note that Tamargo *et al.* (1988) have inferred from reflection electron diffraction measurements that 2d growth can be achieved on the GaAs(100) 2x4 surface. This is an important step which must be pursued and clarified.

It has been shown empirically that much more uniform MBE growth of ZnSe on GaAs (100) occurs by initiating deposition in a Zn−rich regime (DePuydt *et al.*, 1987; Gaines *et al.*, 1993; Guha *et al.*, 1993). This would seem to be in keeping with an α(4x2) surface reconstruction suggested by Farrell *et al.* (1988) and consistent with early STM images of the 4x2 surface (Biegelsen *et al.*, 1990). However, total energy calcu-

calculations (Northrup and Froyen, 1994) again predict that the most stable surface structure should be the $\beta 2(4x2)$ phase, with only 3/4 ML As below the Ga-Ga dimers, and more recent STM experiments (Skala *et al.*, 1993) are interpreted to imply non-$\alpha(4x2)$ arrangements. Further work is clearly necessary to study the Zn-rich initiation of ZnSe on Ga-rich GaAs (100) surfaces.

Conclusions

In summary, Se reactivity with Si and GaAs substrates leads to disruption of ideal heteroepitaxy. In the case of Si(100), an adsorbed As ML both passivates the Si surface and acts as well as an ideal interfacial buffer for II-VI overgrowth. Currently, a similarly strong mechanism has not been observed for stage to stage control of ZnSe growth on GaAs(100). However, STM measurements coupled with photoemission spectroscopy should elucidate the tendency toward uniform growth when Zn is dominant during the growth initiation.

References

Biegelsen DK, Bringans RD, Northrup JE, Swartz L-E (1990) Surface reconstructions of GaAs(100) observed by scanning tunneling microscopy. Phys Rev B **41**, 5701-5706.

Biegelsen DK, Bringans RD, Northrup JE, Swartz L-E (1994) Selenium- and tellurium-terminated GaAs(100) surfaces observed by scanning tunneling microscopy. Phys Rev B **49**, 5424-5428.

Bressler-Hill V, Wassermeier M, Pond K, Maboudian R, Briggs GAD, Petroff PM, Weinberg WH (1992) Atom-resolved imaging and spectroscopy on the GaAs(001) surface using tunneling microscopy. J Vac Sci Technol B **10**, 1881-1885.

Bringans RD, Olmstead MA (1989) Bonding of Se and ZnSe to the Si(100) surface. Phys Rev B **39**, 12985-12988.

Bringans RD, Biegelsen DK, Swartz L-E, Ponce FA, Tramontana JC (1992) Effect of interface chemistry on the growth of ZnSe on the Si(100) surface. Phys Rev B **45**, 13400-13406.

Chambers SA, Sundaram VS (1991) Passivation of GaAs(001) surfaces by incorporation of group VI atoms: a structural investigation. J Vac Sci Technol B **9**, 2256-2262.

DePuydt JM, Cheng H, Potts JE, Smith TL, Mohapatra SKJ (1987) Growth of undoped ZnSe on (100) GaAs by molecular-beam epitaxy: an investigation of the effects of growth temperature and beam pressure ratio. Appl Phys Lett **62**, 4756-4762.

Farrell HH, Tamargo MC, de Miguel JL (1988) Molecular-beam epitaxy and atomic-layer epitaxy growth mechanisms for ZnSe(100) J Vac Sci Technol B **6**, 767-768.

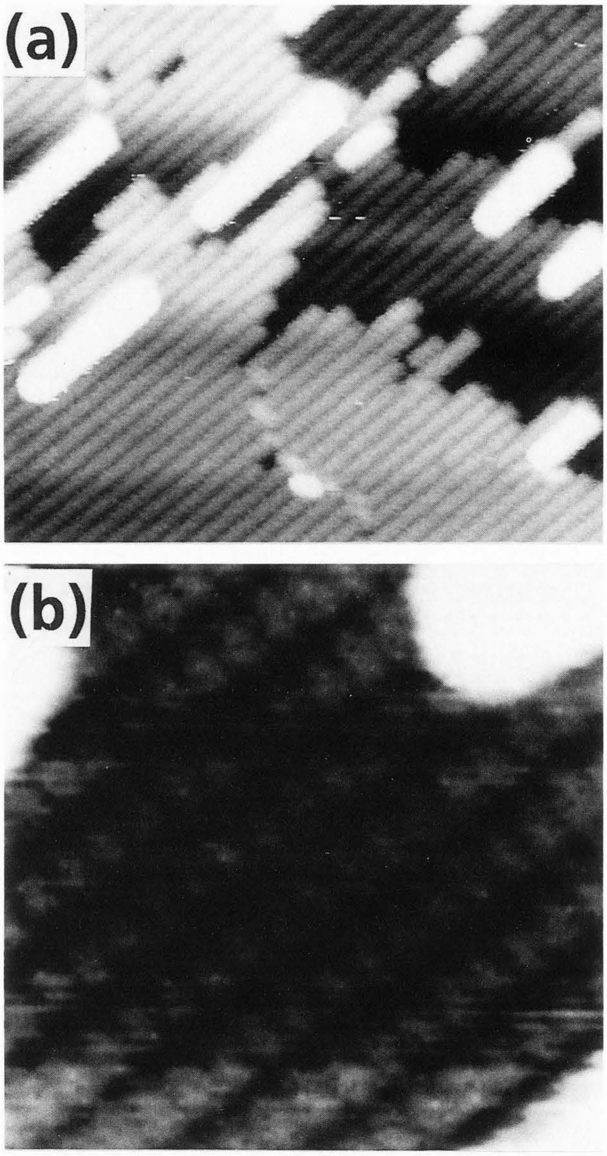

Figure 5. STM filled state, constant current images of GaAs(100):Se surfaces. Lighter gray value indicates higher. **(a)** 11 nm x 12 nm area; **(b)** 3 nm x 3 nm area. (Reprinted from Biegelsen *et al.*, 1994)

Gaines JM, Petruzello J, Greenberg BJ (1993) Structural properties of ZnSe films grown by migration enhanced epitaxy. Appl Phys **73**, 2835-2840.

Guha S, Munekata H, Chang LL (1993) Structural quality and the growth mode in epitaxial ZnSe/GaAs (100). J Appl Phys **73**, 2294-2300.

Harrison WA, Kraut EA, Waldrop JR, Grant WR (1978) Polar hetero-junction interfaces. Phys Rev B **18**, 4402-4410.

Hashizume T, Xue QK, Zhou J, Ichimiya A, Sakurai T (1994) Structures of As-rich GaAs(001) 2x4 reconstructions. Phys Rev Lett **73**, 2208-2211.

Li D, Pashley MD (1994) Interaction of selenium with the GaAs(001)-(2x4)/c(2x8) surface studied by scanning tunneling microscopy. Phys Rev B **49**, 13643-13649.

Northrup JE, Froyen S (1994) Structure of GaAs (001) surfaces: the role of electrostatic interactions. Phys Rev B **50**, 2015-2018.

Park RM, Mar HA (1986) Molecular beam epitaxial growth of high quality ZnSe on (100) Si. Appl Phys Lett **48**, 529-531.

Romano LT, Bringans RD, Knall J, Biegelsen DK, Garcia A, Northrup JE (1994) Atomic rearrangement at the interface of annealed ZnSe films grown on vicinal Si(001) substrates. Phys Rev B **50**, 4416-4423.

Skala SL, Hubacek JS, Tucker JR, Lyding JW, Chou ST, Cheng K-Y (1993) Structure of GaAs(100)-c(8x2) determined by scanning tunneling microscopy. Phys Rev B **48**, 9138-9141.

Takatani S, Kikawa T, Nakazawa M (1992) Reflection high energy electron diffraction and photoemission spectroscopy study of GaAs(001) surface modified by Se adsorption. Phys Rev B **45**, 8498-8505.

Tamargo MC, de Miguel JL, Hwang DM, Farrell HH (1988) ZnSe/III-V heterostructures grown in a multichamber MBE system. J Vac Sci Technol B **6**, 784-789.

Uhrberg RIG, Bringans RD, Bachrach RZ, Northrup JE (1986) Symmetric arsenic dimers on the Si(100) surface. Phys Rev Lett **56**, 520-523.

Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no **Discussion with Reviewers**.