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Bonding of Se and ZnSe to the Si(100) surface

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The interfaces formed when films of Se and ZnSe are deposited on Si(100) substrates have been studied with photoemission core-level spectroscopy. For Se films deposited at room temperature and annealed, the presence of Si atoms with chemical shifts of δ, 2δ, 3δ, and 4δ where δ is 0.53 ± 0.03 eV were found, suggesting the formation of $SiSe_2$. At higher annealing temperatures, the results are consistent with the presence of a submonolayer of Se atoms in bridge sites on the Si(100) surface. ZnSe films were deposited at room temperature and at 300 °C on Si(100) and the primary bonding at the interface was found to be between Si and Se. Island formation occurred in the initial stages of growth at the higher temperature.

In the heteroepitaxy of compound on elemental semiconductors, regular layer-by-layer growth does not always occur. For the much-studied case of GaAs on Si, for example, one of the important effects is the strong bonding of a monolayer of As to the Si substrate at the beginning of growth. This makes it energetically favorable for islands of GaAs to form rather than two-dimensional or layer-by-layer growth of GaAs. In this paper, we examine the bonding of both Se and ZnSe to the (100) surface of Si and find fundamentally different behavior at the interface.

Of the many possible overlayers on semiconductor surfaces, there are several combinations which give rise to simple or unreconstructed surfaces. It has been shown that unreconstructed Ge(111) or Si(111) surfaces can be obtained if the surface layer of Ge or Si is replaced by a layer of As atoms.[1-3] This occurs because the As atoms have one extra valence electron compared to Ge or Si atoms, and thus the partially occupied surface orbitals for the clean surfaces are replaced by a fully occupied or lone-pair orbital. A monolayer of arsenic atoms has also been shown to provide a passivated coverage on the Si(100) surface.[4] In this case, the Si-Si dimers of the clean surface reconstruction are broken and As-As dimers are added on top. The extra valence electron on each As atom again leads to fully coordinated atoms.

A similar argument about fully coordinating the surface atoms holds for group VI atoms on Si(100). In this case a Se atom, for example, could form a bridge bond between two adjacent Si atoms. All of the Se and Si atoms would then be fully coordinated resulting in a 1×1 surface symmetry. Core-level spectroscopy investigations have been carried out for monolayers of S on Si(100) (Ref. 5) and S on Ge(100) (Ref. 6). Only Ge(100):S has been obtained in an ordered state, and for this system detailed core-level photoemission measurements have shown that the S atoms are indeed in bridge sites and that the low-energy electron diffraction (LEED) pattern has a 1×1 symmetry. Angle-resolved photoemission spectroscopy measurements[7] on this surface have shown the presence of a strongly dispersing sulfur-induced band in the energy range 2–4 eV which was identified as being due to the nonbonding lone-pair states on the S atoms. Recent normal emission angle-resolved photoemission fine-structure measurements[8] are also consistent with the S atoms being in a bridge site on Ge(100).

We will present results for the interface formed between Se and Si(100) and between ZnSe and Si(100). The clean surfaces and interfaces were studied using ultraviolet photoemission spectroscopy (UPS), LEED, and soft x-ray core-level spectroscopy (CLS). We will emphasize the CLS results here because they provide direct information about bonding at the interface. In particular, we will focus on the chemical shifts of the Si $2p$ core level because these represent bonding at the interface. In order to facilitate the identification of the chemical shifts, a spin-orbit deconvolution was carried out. This requires no curve fitting but is a numerical manipulation of the spectra, having only the spin-orbit splitting and spin-orbit ratio as inputs.[9] Statistical spin-orbit ratios and splittings of 0.605 and 0.858 eV for the Si $2p$ and Se $3d$ lines, respectively, were used.

The Si(100) substrates (0.01 Ω cm, boron doped) were prepared by forming a thin sacrificial oxide layer outside the vacuum chamber[10] and then annealing it off in the growth chamber. Selenium was produced using an electrochemical cell[11] and the ZnSe films were prepared by evaporation from solid ZnSe. Film thicknesses were determined with a quartz-crystal monitor which was held at 25 °C. The samples were transferred in UHV to the analysis chamber and CLS measurements were carried out at the Stanford Synchrotron Radiation Laboratory using a cylindrical mirror analyzer. A range of photon energies was used but all of the data presented here were taken at 130 eV, which provides surface sensitivity for the Si $2p$ core level.

Solid Se has a high vapor pressure at relatively low temperatures, and so Se films were deposited at room temper-

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ature (RT) and then annealed to produce thin layers. After annealing for 2 min at 150 °C, the Si core level showed a bulklike peak and considerable intensity in chemically shifted components. As the film was annealed at higher temperatures, the ratios of these shifted components changed, as will be discussed below. Examples of the Si $2p$, Si $2p_{3/2}$, and Se $3d_{5/2}$ spectra are shown in Fig. 1 along with results of fitting the Si $2p$ spectra. Spin-orbit deconvolution of the data was carried out to make the chemical shifts more recognizable, but the fits were made to the full spectra. The fits were carried out using convolved Lorentzian and Gaussian peak shapes. For each fit, the number of peaks (one bulk, plus four shifted), the spin-orbit splitting (0.605 eV), and the spin-orbit ratio (2:1) were fixed, the peak widths were constrained to be equal, and only amplitudes and peak positions were allowed to vary for individual peaks. A much poorer fit could be obtained for some of the spectra using fewer peaks, but the important result found was that a free fitting using one bulk and four shifted peaks always gave approximately equal separations. This behavior, with chemical shifts of 1–4 times 0.53 ± 0.03 eV for Si(100):Se, is similar to the results of Weser *et al.* for Si(100):S where shifts of 1–4 times 0.62 eV were found.[5] Both results are strongly suggestive of Si atoms bonded to 1–4 atoms of S or Se and are indicative of the formation of the compounds SiS_2 and $SiSe_2$ in which each Si atom is surrounded by four S or four Se atoms (in analogy with SiO_2). We will label the chemical shifts as 1δ, 2δ, etc. The 4δ shift corresponds to $SiSe_2$ and the 1δ, 2δ, and 3δ shifts correspond to Si atoms nearer the interface with fewer bonds to Se atoms.

The uppermost set of spectra in Fig. 1 corresponds to a Se film on Si(100) which has been annealed to 300 °C. The undeconvolved Si $2p$ spectrum shows a large intensity at large chemical shifts. In the deconvolved Si $2p_{3/2}$ spectrum, significant intensity is seen in all of the shifted components. After further anneals, the intensity in the 3δ and 4δ states is reduced, as can be seen in the central set of spectra in Fig. 1. [A similar result, shown in the lowermost panel in Fig. 1, is found after ZnSe films on Si(100) have been annealed to temperatures of about 500 °C. This leaves some Se atoms but no Zn atoms on the surface]. The ratio of the intensity in the $3\delta+4\delta$ states to that in the $1\delta+2\delta$ states is shown in Fig. 2 as a function of annealing temperature for a Se film on Si(100). These results are consistent with $SiSe_2$ formation at the early stages and then a monolayer or submonolayer of Se at the higher annealing temperatures. The initial decrease of the Se/Si ratio is due to Si moving closer to the surface as $SiSe_2$ is formed. Note that the minimum in the Se/Si ratio occurs near the maximum for $SiSe_2$ (as shown by the $3\delta+4\delta$ components). At higher temperatures, the Se evaporates leaving Si bonded only to one or two Se atoms. A complete monolayer of Se atoms in bridge sites would give 2δ only and a submonolayer would give 2δ and 1δ components. The spectra for the higher annealing temperatures show approximately equal intensity in the 1δ and 2δ states. This is consistent with the presence of $\frac{3}{4}$ of a monolayer of Se atoms in bridge sites, because one missing Se atom will leave two Si atoms in a 1δ state. The LEED and UPS results are also consistent with this result. The 2×1 LEED pattern and the strong surface state in UPS seen for the clean surface were replaced for the submonolayer Se film by a 1×1 pattern and the absence of any surface states near the top of the valence band. The transition from a thick Se film to $SiSe_2$ to submonolayer coverage is shown schematically in Fig. 3.

We now move to the interface formed when ZnSe is grown on Si(100). Thin ZnSe films have been grown on Si (see Refs. 12 and 13, for example) and GaAs substrates[14] using molecular-beam epitaxy. Evaporation from both elemental sources[12,13] and compound ZnSe

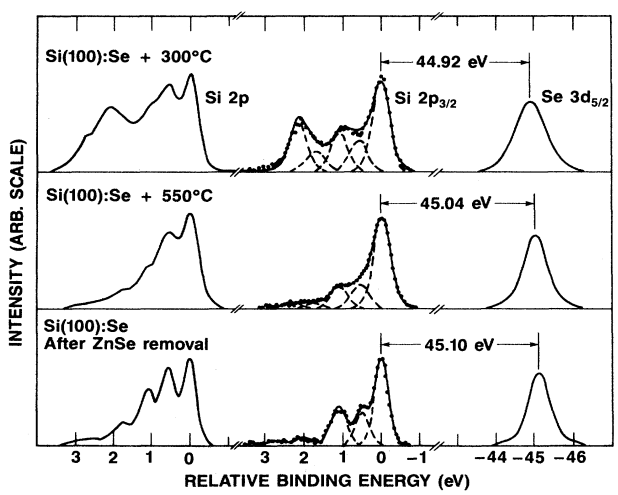

FIG. 1. Si $2p$, Si $2p_{3/2}$, and Se $3d_{5/2}$ core-level spectra for Si(100):Se surfaces taken with $h\nu = 130$ eV. Spectra in the top (center) panel correspond to a film deposited at RT and then annealed at a number of temperatures up to a maximum of 300 °C (550 °C). Spectra in the bottom panel are for a ZnSe film on Si(100) which was annealed until all the Zn but not all of the Se was desorbed. For the case of the Si $2p_{3/2}$ spectra, data points are shown as dots and the results of fitting are shown by the solid and dashed lines.

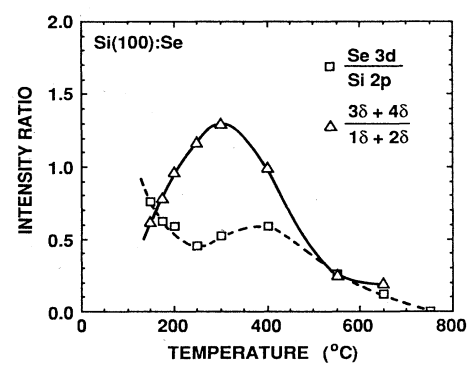

FIG. 2. The ratio of intensity in the Se $3d$ core level to that in the Si $2p$ level for a Se film deposited at RT and then annealed for 2 min at each of a number of temperatures (dashed line). The ratio of intensity in the 3δ and 4δ shifted components of the Si $2p$ core level to that in the 1δ and 2δ components is shown by the solid line.

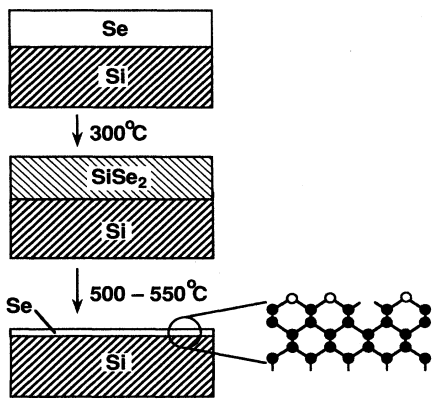

FIG. 3. Schematic diagram showing the effect of annealing a thick film of Se on Si(100). After annealing to 500–550 °C, only a submonolayer of Se remains.

sources[14] has been successful, with dissociation into Zn and Se_2 molecules occurring in the latter case. In both cases, the optimum substrate temperature for good ZnSe crystal quality has been found to be in the range 300–350 °C. At these temperatures, a Se (Zn) atom has a nonzero sticking coefficient only if it can bond to a Zn (Se) atom, and the growth rate is determined by the arrival rate of the minority species.[13] In the present study a compound source was used and layers 1.0 and 3.0 nm thick (as determined by a room-temperature crystal monitor) were deposited on a Si(100) substrate held at room temperature and also on a substrate held at 300 °C.

The Si $2p$, Se $3d$, and Zn $3d$ core levels were measured for these films. Core-level intensity ratios are shown in Fig. 4 for two of these films and are compared with those for the Si(100):Se case discussed previously. Before any further annealing, the 1.0-nm RT film has the appearance of greater thickness than the 3.0-nm, 300 °C film (i.e., larger Se/Si and Zn/Si ratios). This suggests that ZnSe islands form and/or reevaporation of the incoming Zn atoms and Se_2 molecules occurs at the higher substrate temperature. Island formation is favored because after annealing the RT-deposited films, we observe a decrease in the Se/Si intensity ratio. This effect cannot be due to reevaporation of ZnSe because the ZnSe vapor pressure is negligible at these temperatures. The Se/Si ratio for the 3.0-nm, 300 °C film is significantly greater than that for the Se only film, while the Zn/Se ratio is far less than that for the presumably uniform and stoichiometric RT film. Hence, if island formation takes place, there is Se between the islands. If, on the other hand, reevaporation, but no island formation has occurred, then there must be a uniform coverage of more than one ZnSe monolayer to explain the value of the Se/Si intensity ratio that is measured.

The Si $2p_{3/2}$ spectra for ZnSe on Si(100) should give information about bonding at the interface. Figure 5 shows results for the 1.0-nm, RT, and 3.0-nm, 300 °C films, both as-deposited and after anneals of around 500 °C. All spectra have considerable intensity shifted to higher binding energy, suggestive of Si—Se bonding.

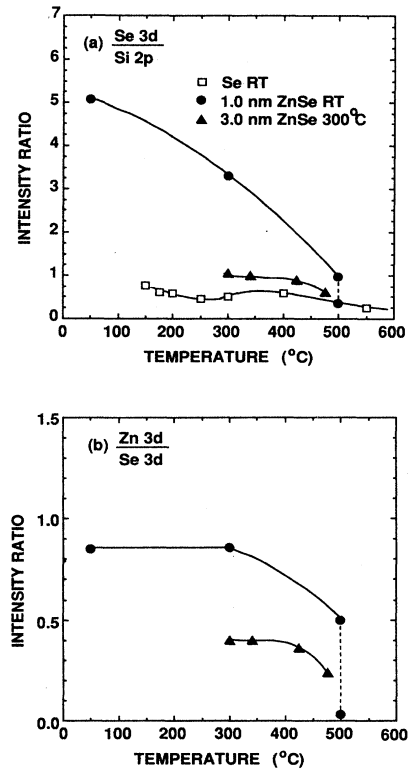

FIG. 4. Intensity ratios (a) Se $3d$/Si $2p$ and (b) Zn $3d$/Se $3d$ as a function of annealing temperature for ZnSe films on Si(100). Data are shown for a 1.0-nm film deposited at RT and a 3.0-nm film deposited at 300 °C. All anneals were for 2 min except for a second 5-min anneal at 500 °C for the 1.0-nm film. Comparable data for a Se film from Fig. 2 are shown for comparison.

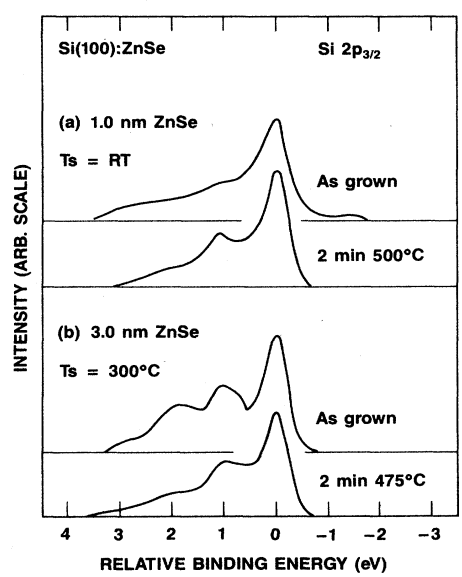

FIG. 5. Si $2p_{3/2}$ spectra for (a) a 1.0-nm film of ZnSe deposited at RT and (b) a 3.0-nm film of ZnSe deposited on Si(100) at 300 °C.

There is evidence of a small amount of Zn−Si bonding (shifts to lower binding energy) for the as-deposited RT film, but this disappeared after a 300 °C anneal. Spectra for the as-deposited films show significant intensity at shifts equivalent to those labeled 3δ and 4δ for the Se on Si(100) case. This is particularly evident for the film deposited at 300 °C where large intensity is seen at 3δ and 4δ. This result is more consistent with $SiSe_2$ formation between ZnSe islands on the surface than with the formation of a uniform ZnSe film, because the latter alternative requires a thick $SiSe_2$ layer below the ZnSe film.

Sustained annealing of all of the thin ZnSe layers we have examined leads to a complete loss of Zn atoms before all of the Se is lost, and as shown in Fig. 1, similar Si $2p_{3/2}$ spectra to those corresponding to a submonolayer of Se on the Si(100) surface are found. That is, the $(3\delta+4\delta)/(1\delta+2\delta)$ ratio is small.

In summary, for Se films deposited at RT on Si(100) surfaces, $SiSe_2$ compound formation occurs after annealing to 300 °C. After annealing to higher temperatures, a submonolayer of Se atoms in bridge sites remains. Films of ZnSe deposited at 300 °C on Si(100) most likely form as islands with Se and/or $SiSe_2$ between the islands. It is also possible that reevaporation of Zn and Se_2 molecules during growth slows down the growth rate of the ZnSe. If island formation does not occur, then the bonding is mainly between Si and Se. If islanding does occur then (i) Si−Zn bonding may be "hidden" under islands and (ii) the degree of islanding is not as pronounced for RT deposition followed by a 300 °C anneal as it is for deposition at 300 °C. In all cases, annealing to around 500 °C removed all Zn atoms and left a similar submonolayer of Se to that seen for Si(100):Se.

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[1]R. D. Bringans, R. I. G. Uhrberg, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **55**, 533 (1985).

[2]M. A. Olmstead, R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **34**, 6041 (1986).

[3]R. I. G. Uhrberg, R. D. Bringans, M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. B **35**, 3945 (1987).

[4]R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).

[5]T. Weser, A. Bogen, B. Konrad, R. D. Schnell, C. A. Schug, and W. Steinmann, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, Sweden, 1986,* edited by O. Engström (World Scientific, Singapore, 1987), pp. 97–100.

[6]T. Weser, A. Bogen, B. Konrad, R. D. Schnell, C. A. Schug, and W. Steinmann, Phys. Rev. B **35**, 8184 (1987).

[7]T. Weser, A. Bogen, B. Konrad, R. D. Schnell, C. A. Schug, W. Moritz, and W. Steinmann, Surf. Sci. **201**, 245 (1988).

[8]K. T. Leung, L. J. Terminello, Z. Hussein, X. S. Zhang, T. Hayashi, and D. A. Shirley, Phys. Rev. B **38**, 8241 (1988).

[9]Details are given by R. D. Bringans, M. A. Olmstead, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **36**, 9569 (1987).

[10]B. S. Krusor, D. K. Biegelsen, R. D. Yingling, and J. R. Abelson, J. Vac. Sci. Technol. B **7**, 129 (1989).

[11]W. Heegemann, K. H. Meister, E. Bechtold, and K. Hayek, Surf. Sci. **49**, 161 (1975).

[12]N. Mino, M. Kobayashi, M. Konagi, and K. Takahashi, J. Appl. Phys. **58**, 793 (1985).

[13]R. M. Park and H. A. Mar, Appl. Phys. Lett. **48**, 529 (1986).

[14]See, for example, R. M. Park and N. M. Salansky, Appl. Phys. Lett. **44**, 249 (1984).