Interface structure of ZnS/Si(001) and comparison with ZnSe/Si(001) and GaAs/Si(001)

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(Received 8 March 1995; revised manuscript received 19 June 1995)

The interface between ZnS and Si(001) has been studied with transmission electron microscopy. It was found that stacking faults were the dominant microstructural defect in the ZnS films. Higher-quality interfaces and better ZnS films were obtained when arsenic-terminated Si(001) surfaces were used as the substrate. It was also found that the stacking fault density was much lower and qualitatively different than for interfaces formed without an As monolayer. Stacking faults in only one of the two possible orientations were observed for ZnS grown on non-As-terminated Si(001). These results are compared with those for ZnSe on Si and GaAs on Si and it is concluded that lattice match does not play as large a role as does chemical compatability at the interface.

I. INTRODUCTION

The growth of compound semiconductors on Si substrates has been investigated because of the interest in combining optoelectronic properties with very large scale integration technology. Most of the earlier work involved GaAs films grown on Si, and more recently II-VI semiconductor growth on Si has been investigated (see, for example, Refs. 1 and 2). It was initially thought that lattice mismatch was the major effect that made good quality heteroepitaxy difficult, but results for the small lattice mismatch system GaP/Si (0.33% mismatch) have been found to be not much different qualitatively[3] from those for the large lattice mismatch system GaAs/Si (4.1% mismatch). The results that we describe here also show that ZnSe/Si (4.4% mismatch) is much more similar to ZnS/Si (−0.40% mismatch) than it is to GaAs/Si despite the fact that GaAs and ZnSe have similar lattice constants. These comparisons indicate that in compound growth on Si the chemistry at the interface plays a more dominant role than the lattice mismatch. As we will describe below, the problem of interface chemistry can be understood with simple electron counting arguments that show that an abrupt interface between Si and a compound semiconductor is energetically unfavorable. In addition, reactivity between the overlayer species and the substrate atoms can cause the formation of a compound at the interface or lead to etching of the substrate if some of the reactants are volatile. This latter effect is seen[4] in the growth of several II-VI compounds grown on Si.

Previous results for both ZnSe/Si(001) (Ref. 1) and ZnS/Si(001) (Ref. 2) have found evidence that the presence of an As monolayer at the interface leads to a better quality overlayer. This can be understood in terms of the following electron counting argument:[5] In bulk ZnSe, each Zn (S) atom contributes $\frac{1}{2}$ ($\frac{3}{2}$) electrons to each of the four bonds surrounding it and in bulk Si each atom contributes exactly one electron per bond. At a (001) interface between Si and the Zn plane of ZnS, therefore, the interface bonds will each receive a total of $\frac{3}{2}$ electrons instead of the two electrons required. This situation is shown schematically in Fig. 1(a). [If, on the other hand, the interface is formed between Si and the S plane of ZnS, then a total of $\frac{5}{2}$ electrons per interface bond would result as is shown in Fig. 1(b).] If, however, there is an As monolayer between the Zn layer and the Si, in the sequence Si-Si-As-Zn-S-Zn-S, the As layer has five electrons per atom and can contribute 1 electron to each of the two Si atoms below it and $\frac{3}{2}$ electrons to each of the two Zn

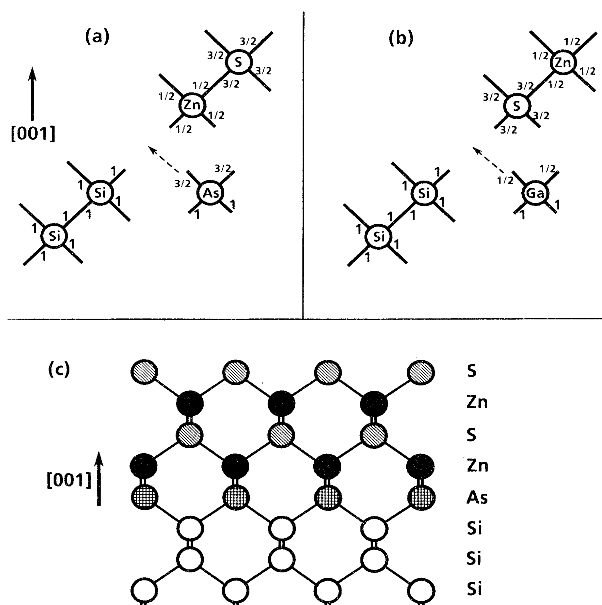

FIG. 1. Bonding configuration at ZnS/Si(001) interfaces. The numbers represent the number of electrons contributed to each of the bonds. (a) Shows that an interface with the sequence Si-Si-Zn-S-Zn will have interface bonds with a total of $\frac{3}{2}$ electrons, whereas the insertion of an As monolayer can leave all bonds with two electrons. (b) Shows that for a Si-Si-S-Zn-S sequence there will be a total of $\frac{5}{2}$ electrons in the interface bond and that insertion of a monolayer of Ga atoms allows this interface to achieve two electrons per atom. (c) Shows the schematic crystal structure of ZnS/Si(001):As.

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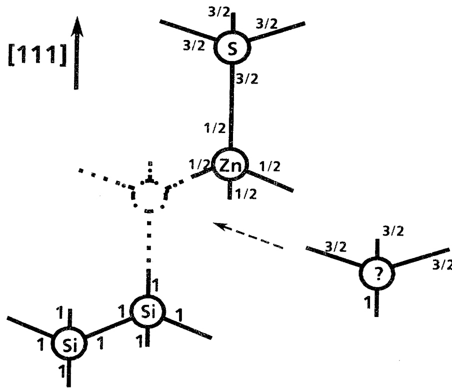

FIG. 2. Bonding configuration at the ZnS/Si(111) interface. It is not possible to achieve two electrons per interface bond with a monolayer of one species. The example shows that for the configuration where (i) the Si surface has one bond crossing the interface and (ii) the Zn layer of ZnS is at the interface, a matching layer with $\frac{11}{2}$ electrons would be necessary.

atoms above it so that all of the bonds have two electrons [see Fig. 1(a)]. The interface structure for this situation is shown in Fig. 1(c). Figure 1(b) shows the analogous case where a monolayer of Ga between Si and the sulfur plane of ZnS also satisfies electron counting.

Matching monolayers such as these are not available for all II-VI/IV interfaces; we note, for example, that an As monolayer does not satisfy the electron counting for {111} interfaces where there are either one or three bonds crossing the interface plane for each Si atom. Monolayers with $\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$, or $\frac{11}{2}$ valence electrons would be needed depending on whether Zn or S is at the interface and whether there are one or three bonds per interface Si atom. One example is shown in Fig. 2, where we see that $\frac{11}{2}$ valence electrons are needed per interface atom. This could be achieved, however, by a monolayer consisting of 50% S and 50% As.

An analogous argument shows that a single matching monolayer does not work for GaAs/Si(001) either, but that a layer consisting of 50% Ga and 50% Si bonded to the As plane of GaAs(001) [or of 50% As and 50% Si bonded to the Ga plane of GaAs(001)] will satisfy the electron counting requirement. Mixed monolayers such as these are difficult to achieve in practice because growth tends to be carried out under excess As conditions that lead to termination of Si by a full monolayer of As. The Si(001):As monolayer termination, which is so advantageous for ZnSe growth on Si(001), thereby causes problems in the growth of GaAs on Si(001).

In this paper we present results of a TEM study of the interface between ZnS and Si(001). We look both at the special case where there is an As monolayer as described above, and at the interface without the As layer and compare the results with those for ZnSe on Si and GaAs on Si.

II. EXPERIMENT

Epitaxial ZnS films were grown on Si(001) and arsenic-passivated Si(001) substrates that were offcut 4° towards the [$\bar{1}$10] axis in a VG V80S molecular beam epitaxy system equipped with a 15-keV reflection high-energy electron diffraction (RHEED) system and a residual gas analyzer system. The substrates were chemically wet etched and then annealed in the growth chamber at a temperature of 870 °C for 20 min to remove surface oxides. Annealing a clean vicinal Si(001) surface above 800 °C before growth gave predominantly double-height steps with the Si-Si dimer direction and the step edges parallel to the [110] direction. [See inset in Fig. 3(a)]. A compound source of ZnS was used for film growth[2] and an elemental source of As for passivation using procedures established earlier.[1] Double stepped Si(001):As 2×1 and Si(001):As 1×2 with As-As dimers parallel and perpendicular, respectively, to the surface steps were obtained depending on the substrate temperature. RHEED indicated that the As-As dimers broke up when both Zn and S atoms were present at the beginning of the growth. ZnS layers were grown in two steps within initial substrate temperature of 220 °C and a beam flux pressure of 1×10^{-7} mbar for 5 min followed by a substrate temperature of 300 °C and a beam flux pressure of 1×10^{-6} mbar. For ZnS grown on As-passivated surfaces, sulfur dimers were observed by RHEED to form in the same direction as the As dimers.[2] For films discussed in this paper the As (S) dimer direction was perpendicular to the surface step edges for films grown on As-passivated Si(001). Secondary-ion mass spectroscopy (SIMS) profiles indicated that the As remained in the interface region. The film thickness was about 300 nm.

Cross-sectional TEM samples were prepared by cutting and polishing slices parallel to the [1$\bar{1}$0] and [110] directions as referenced to the ZnS lattice and the Si surface steps. The [110] direction is perpendicular to the S dimers for the films grown on Si(001):As. The polished samples were thinned to electron transparency on a liquid-nitrogen cold stage using Ar-ion milling at 3 keV to minimize ion damage. Conventional electron microscopy and high-resolution (HREM) images were taken using a JEOL 3010 high-resolution microscope at 300 kV.

III. RESULTS

Figures 3(a) and 3(b) are respectively low- and high-magnification cross-sectional TEM images of a 300-nm ZnS film on a vicinal Si(001) surface taken with the electron beam parallel to the step edges, i.e., in the [110] direction. The lower-magnification image in Fig. 3(a) shows a high density of stacking faults that extend from the interface to the film surface in only one of the two possible stacking fault orientations possible in this cross section. The width of the stacking faults can be determined from the HREM image in Fig. 3(b) to be about 2–3 {111} lattice planes ($\sim$1 nm). The inset in Fig. 3(b) is the diffraction pattern of the [110] zone of the ZnS crystal. The pattern shows sharp streaks through only one set of {111} diffraction spots, indicating a single orientation of very thin (1$\bar{1}$1) stacking faults present in the film in this direction.

The orientation of the stacking faults relative to the surface steps is similar to that found[1] for ZnSe on Si(001).

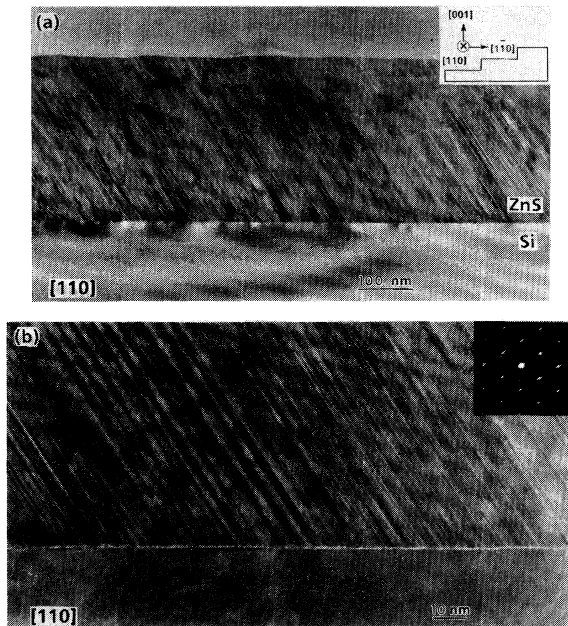

FIG. 3. (a) Low-magnification electron micrograph of a ZnS film grown on Si(001) taken with the e^- beam parallel to the [110] direction. The inset shows the sign convention used for labeling with respect to the stepped interface. (b) HREM of the same film in the [110] direction. The inset is the [110] diffraction pattern of the ZnS showing streaks through the $(1\bar{1}1)$ set of diffraction spots corresponding to $(1\bar{1}1)$ stacking faults.

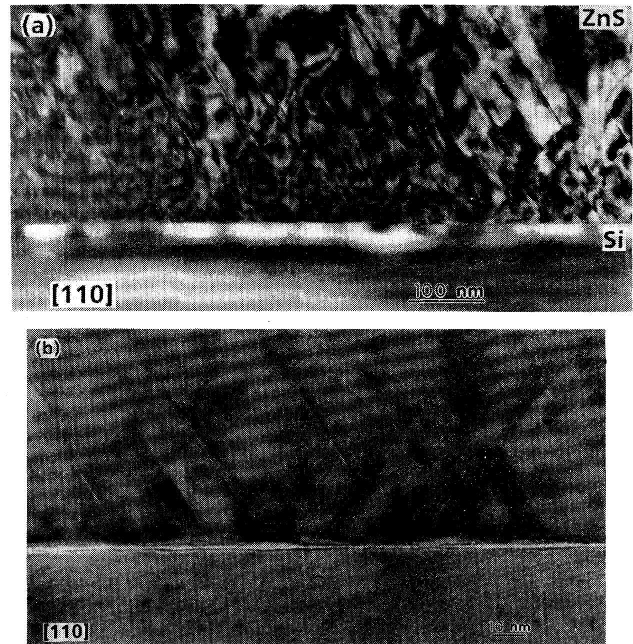

FIG. 4. (a) Low-magnification electron micrograph of a ZnS film grown on arsenic-passivated Si(001) with the electron beam parallel to the [110] direction. (b) HREM of the same film in the [110] direction.

Anisotropy of the stacking faults has also been seen in GaAs on Si(001) grown at low substrate temperatures (see Refs. 6 and 7, for example) but in that case the orientational seems to depend on details of the growth conditions. We note that the stacking fault separation seen here for ZnS was smaller than that found in both GaAs and ZnSe. A small tilt of the ZnS crystal relative to the Si substrate crystal of $<0.5°$ can also be observed in the HREM image. This is similar to GaAs films grown on vicinal Si(001), where tilts varied between 0.05° and 0.3° depending on the details of growth,[8–11] and ZnSe grown on vicinal Ge(001) where the tilt was[12] 0.5°. In all of these cases, the tilt observed was much smaller than the case of ZnSe/Si(001) where the tilt was found[1] to be 5°. Table I summarizes these comparisons for film structures observed parallel to the surface step edges, along with lattice mismatch and growth temperature. A comparison is also made with more standard GaAs/Si(001) growth conditions[13] and stacking fault formation energies.[14]

Cross-sectional TEM images of ZnS films grown on an arsenic-passivated Si(001) surface are shown in Figs. 4(a) and 4(b) with the electron beam also parallel to step

TABLE I. Comparison of material parameters and stacking fault (SF) orientations and spacings along the [110] orientation of ZnS, ZnSe, and GaAs films grown on Si(001)and Si(001):As. In all cases the substrates were offcut 4° towards the $[\bar{1}10]$ axis. Where two growth temperatures are shown they are for buffer layer and remaining film growth, or in the case of ZnSe/Si(001), for deposition temperature and regrowth annealing temperature. Blank table entries indicate that the measurement was not made. (A single asterisk denotes a total film thickness of 0.1 μm. A double asterisk denotes a total film thickness of 0.5 μm.)

	Growth temperature (°C)	Lattice mismatch (%)	Crystal alignment	SF orientation at interface ↖ $\equiv[\bar{1}11]$ ↗ $\equiv[1\bar{1}1]$	SF separation at interface (nm)	SF separation at surface of 0.2 μm film (nm)	SF energy mJ/M^2 (meV/atom) (Ref. 14)
ZnS/Si(001):As	300	−0.40	<0.5°	↖↗	10	100	<6 (<5)
ZnS/Si(001)	220/300	−0.40	<0.5°	↗	1	1	<6 (<5)
ZnSe/Si(001):As (Ref. 1)	300	4.4	<0.5°	↖↗	10		13±1 (11±1)
ZnSe/Si(001) (Ref. 1)	50/500	4.4	5°	↗	2.5	2.5*	13±1 (11±1)
ZnSe/Ge(001) (Ref. 12)	330	0.19	0.5°				13±1 (11±1)
GaAs/Si(001) (Ref. 6)	300/600	4.1	<0.5°	90% ↗		110	55±5 (47±5)
GaAs/Si(001) (Ref. 7)	340	4.1	<0.5°	↖		<20**	55±5 (47±5)
GaAs/Si(001) (Ref. 13)	500/600	4.1	<0.5°	↖↗	16	100	55±5 (47±5)

edges. The low-magnification image in Fig. 4(a) shows a much lower ZnS stacking fault density compared to the film grown without an As-passivating layer. Near the interface, stacking faults with both $(\bar{1}11)$ and $(1\bar{1}1)$ orientations are now found with comparable probability. The faults that extend to the surface are still predominantly $(1\bar{1}1)$ faults, but in contrast to the results in Fig. 3, the stacking fault separation at the surface has now increased to about 100 nm. The HREM image in Fig. 4(b) shows that the spacing of the faults at the interface has increased to about 30–40 $\{111\}$ planes (~ 10 nm). A small tilt ($<0.5°$) was also observed in the ZnS relative to the Si. These results are similar to ZnSe grown on Si(001):As substrates and GaAs on Si(001) grown at higher substrate temperatures as summarized in Table I.

IV. DISCUSSION

A. ZnS on Si(001) and Si(001):As

The high stacking fault density in the ZnS grown on Si(001) compared to ZnS grown on Si(001):As may be attributed to a more disordered interface in the initial growth stage. RHEED analysis[15] showed island formation during the initial stages of ZnS growth on Si(001) compared to the nearly two-dimensional growth for ZnS on Si(001):As. Adsorption measurements[15] found that both Zn and S stick effectively to the Si(001) surface in the absence of As. Therefore the interface contains dipoles associated with the Zn-Si and S-Si bonds. This suggests that atomic rearrangement at the interface must occur to maintain local charge neutrality. An atomic rearrangement such as this could have led to the observed island formation. (Island growth in this case serves to achieve electrostatic stability rather than solely to reduce strain as is the case in systems with a large lattice mismatch.) It is most likely that the islands formed here would be strained because of the mixed bonding of the Zn, S, and Si atoms, and that strain is relieved by the formation of stacking faults (especially given the low energy of formation of stacking faults in ZnS).

In the case of ZnS growth on As-terminated surfaces, the reduced number of stacking faults is attributed to the well-ordered initial layer of As-Si and the low-energy interface (from the electron counting arguments of Sec. I). RHEED analysis[15] indicated two-dimensional growth and x-ray diffraction[15] (XRD) measurements showed a 30% improvement in the peak width of the ZnS(004) reflection for films with an As monolayer, indicating higher crystal quality. Thermal desorption[15] and RHEED[2] experiments verified the presence of a sulfur stabilized ZnS surface on the As overlayer suggesting a fully coordinated interface structure of -Si-Si-As-Zn-S-Zn-S. Capacitance-voltage measurements[16] showed a much lower density of interface states for As-passivated interfaces compared to those without As. These measurements indicate an ordered and electrostatically stable surface resulting in a more uniform growth of ZnS with fewer stacking faults. Since the stacking faults form in both the $(1\bar{1}1)$ and the $(\bar{1}11)$ directions, they can annihilate, allowing their density to be decreased further. The slight predominance of $(1\bar{1}1)$ faults extending to the surface, however, may still be a result of the additional misfit and thermal stress on the $(1\bar{1}1)$ planes on the tilted interface.

We found that the ZnS crystal structure was not strongly tilted with respect of the substrate for films grown on either Si or Si(001):As. As discussed below, this is different from ZnSe films grown on non-As-terminated Si(001).

B. Comparison with ZnSe on Si and GaAs on Si

There is a strong similarity in film structure between ZnS and ZnSe grown on Si(001) and between ZnS and ZnSe grown on Si(001):As despite the difference in lattice mismatch. The stacking fault orientation on the unpassivated, stepped Si surface was very similar for ZnS and ZnSe, but with a slightly lower stacking fault density in the ZnSe case, probably due to the higher stacking fault energy of ZnSe compared to ZnS (see Table I). The stacking fault structure and density at the interface for ZnS and ZnSe films on As-passivated Si(001) were essentially identical. Two-dimensional growth was also observed[17] by TEM for ZnSe on Si(001):As. This suggests a strong lowering of the interfacial energy due to the completely coordinated As-Si bonds at the interface as described above using electron counting arguments.

We now turn to the observation that there is a preferential formation of $(1\bar{1}1)$ stacking faults on the tilted surface. A stacking fault asymmetry has also been seen in GaAs/Si(001) and seems to be dependent on growth temperature, being more pronounced at lower temperatures. A predominance of $(1\bar{1}1)$ faults[6] was observed in one study and a predominance of $(\bar{1}11)$ faults[7] in another. [Here, and throughout the paper, we use the labeling convention shown in the inset of Fig. 3(a) so that the upwardly pointing normal to the predominant stacking fault plane points up the steps in the cases of ZnS/Si(001), ZnSe/Si(001), and Ref. 6 for GaAs/Si(001) and down the steps for GaAs/Si(001) in Ref. 7.] Wei and Aindow[7] analyzed their results in terms of a higher resolved shear stress on the $(\bar{1}11)$ planes because of the vicinal surface. However, the fact that the predominant fault orientation is different for the two GaAs studies indicates that the stress argument alone cannot explain the results. This suggests that the different atomic geometries at the interface steps needed for the two different stacking fault orientations may have different energies of formation as discussed by Lao *et al.*[6] This may be related to the observation[18] that the Si(001) substrate temperature for the formation of the first As monolayer during MBE growth has a strong effect on the surface order and structure of the As-As dimers that are formed. In particular, As-As dimers can be oriented either parallel or perpendicular to the substrate step edges depending on the As deposition conditions. Subsequent GaAs growth was found[18] to follow this As-As orientation so that the GaAs [110] crystal direction became oriented either parallel or perpendicular to the substrate tilt direction depending on the deposition conditions. The combination of these results suggests that it is the detailed atomic structure at the interface that gives rise to the asymmetry of the stacking faults. For ZnS/Si(001)

and ZnSe/Si(001) it is again possible that the bonding at the interface steps favors only the $(1\bar{1}1)$ stacking fault orientation.

The only significant difference between ZnS and ZnSe grown on Si(001) is that a 5° tilt was found to occur in the ZnSe films on unpassivated Si surfaces, whereas tilts of less than about 0.5° were found in the ZnS case. For the ZnSe films where the larger tilts were found, however, the growth of single crystalline ZnSe occurred by solid phase regrowth at 500 °C after deposition at 50 °C (carried out to avoid the formation of $SiSe_2$ at the interface). It was suggested[1] that the tilt in ZnSe formed to accommodate the strain between faulted and unfaulted regions of the crystal with the faulted regions arising from parts of the substrate where Se termination gave rise to an unreactive surface. The higher initial growth temperature of 220 °C for ZnS on Si may not allow unreactive regions of the surface to remain during ZnS growth.

V. CONCLUSION

The comparison made here between the compounds grown on Si substrates strongly suggests that lattice match does not play as large a role in the defect structure as does chemical compatibility: ZnSe on Si(001) behaves much more like ZnS on Si(001) than like GaAs on Si(001). This is true for the As-terminated case and also, with the exception of the crystal tilt, for the non-As-terminated case. We also point out that GaP growth on Si(001) (0.33% mismatch) is qualitatively much more similar to GaAs growth on Si(001) (4.1% mismatch) than to ZnS growth on Si(001) (−0.40% mismatch).

ACKNOWLEDGMENTS

X.Z. and W.P.K. acknowledge the technical support of R. Klima and the expert assistance of Dr. B. Gnade, Dr. C. C. Cho, Dr. H. Y. Liu, and Dr. M. Anthony at Texas Instruments for SIMS, XRD analysis, and helpful discussions. The research at Texas A&M was partially supported by the National Science Foundation (ELS-9306293), NASA (NAGW-1184), and the Texas A&M CEMR Research Program (EPR93-85).

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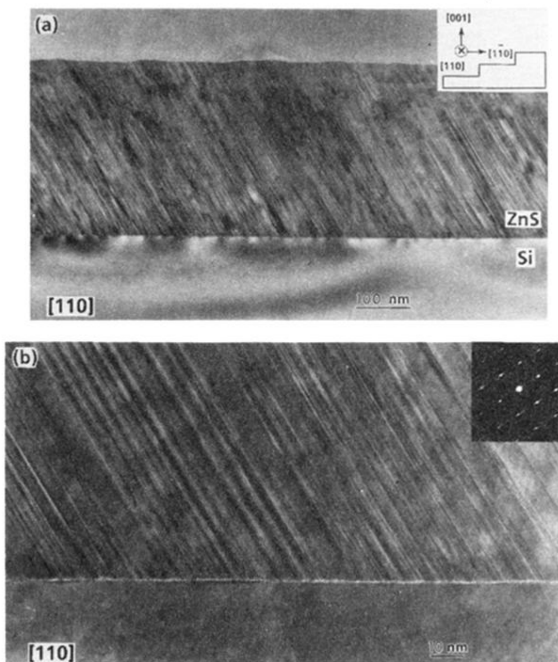

FIG. 3. (a) Low-magnification electron micrograph of a ZnS film grown on Si(001) taken with the e^- beam parallel to the [110] direction. The inset shows the sign convention used for labeling with respect to the stepped interface. (b) HREM of the same film in the [110] direction. The inset is the [110] diffraction pattern of the ZnS showing streaks through the $(1\bar{1}1)$ set of diffraction spots corresponding to $(1\bar{1}1)$ stacking faults.

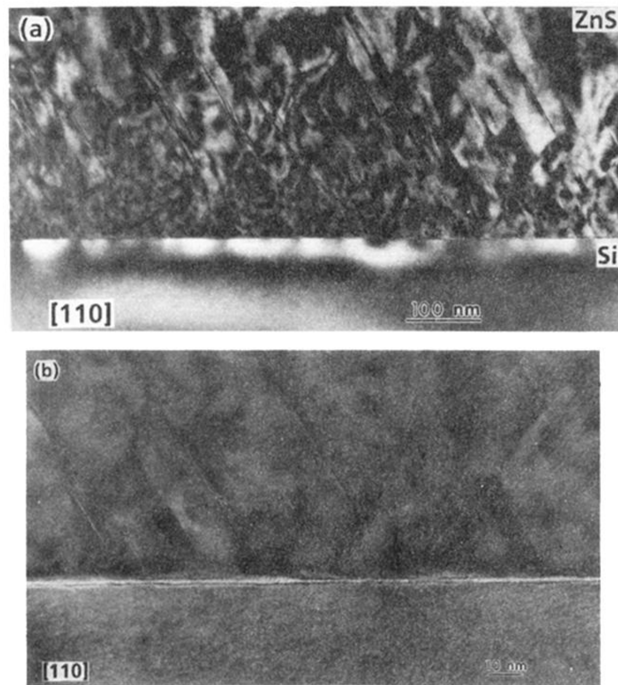

FIG. 4. (a) Low-magnification electron micrograph of a ZnS film grown on arsenic-passivated Si(001) with the electron beam parallel to the [110] direction. (b) HREM of the same film in the [110] direction.