The effect of As passivation on the molecular beam epitaxial growth of high-quality single-domain CdTe(111)B on Si(111) substrates

Y. Xin,[a] S. Rujirawat, N. D. Browning, R. Sporken,[b] and S. Sivananthan
Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60607

S. J. Pennycook
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

N. K. Dhar
U.S. Army Research Laboratory, Adelphi, Maryland 20783-1197

(Received 5 April 1999; accepted for publication 27 May 1999)

The effect of As passivation of Si(111) substrates on the subsequent molecular beam epitaxial growth of CdTe(111) is investigated through a detailed comparison of the microstructures of two types of films. The film grown on a substrate treated with a Te flux is found to exhibit a rough film-substrate interface and has very poor crystalline quality with a (111)A orientation. In contrast, a CdTe film grown under identical conditions except for the Si substrate treated with an As flux is observed to have an atomically abrupt film-substrate interface and a single-domain structure in the technologically more relevant (111)B orientation. A growth mechanism for the formation of these high-quality single-domain CdTe(111)B films is proposed. © *1999 American Institute of Physics.* [S0003-6951(99)03329-X]

The interest in the growth of CdTe on Si is motivated by its potential use as an alternative substrate for the subsequent growth and fabrication of $Hg_{1-x}Cd_xTe$ infrared detectors.[1,2] In this regard, the growth of single-domain CdTe with the (111)B orientation [a short notation for the $(\bar{1}\bar{1}\bar{1})$ Te polar surface, with (111)A denoting the Cd polar (111) surface], is particularly desirable as this orientation requires the least Hg flux for growth of $Hg_{1-x}Cd_xTe$ by molecular beam epitaxy (MBE).[3] This is also the standard orientation for $Hg_{1-x}Cd_xTe$ growth in liquid phase epitaxy, and could be used for CdS/CdTe solar cells grown by MBE.[4] Although CdTe(111) epitaxy has been demonstrated on both Si(001)[5,6] and Si(111) substrates,[7–10] the Si(111) substrate is more attractive because it has the same symmetry as the epitaxial CdTe(111) film. Furthermore, CdTe(111) growth on Si(001) involves a difficult growth process that is plagued by a multidomain problem at the nucleation stage.[11] The direct growth of CdTe on Si(111) is not without problems of its own, having been previously reported to result in the undesirable (111)A orientation.[7,8] The successful growth of (111)B oriented CdTe could only be achieved using Si(111) buffered with $(Ca, Ba)F_2$[9] and GaAs.[10] Most recently single-domain CdTe(111)B has been grown by MBE using a ZnTe buffer layer on a Si(111) substrate passivated by As.[12] However, although the film quality is better than CdTe(111)B grown on Si(001) substrates, the ZnTe buffer layer adds an additional growth stage, and the ZnTe/CdTe interface might act as another source for the generation of threading dislocations.

In this work, we show that the As passivation of the Si substrate is the crucial step for the direct growth of single domain CdTe(111)B films on Si(111) substrates.

Two types of CdTe films were grown directly on nominal Si(111) substrates using a single CdTe cell in a Riber 32 MBE system under the same growth conditions except that the Si substrates were cooled under different flux, i.e., either As flux or Te flux (partial pressure 10^{-7} Torr) from 900 to 400 °C before the CdTe deposition. The growth was initiated at nucleation temperature of 340 °C, then proceeded at the normal growth temperature of 420 °C (thermal couple reading). The growth was monitored by *in situ* reflection high-energy electron diffraction (RHEED). *Ex situ* examination of the films using a variety of imaging and analytical techniques in a JEOL 2010F 200 kV field emission transmission electron microscope (TEM) with the capability to do atomic *Z*-contrast imaging reveals that the two films have radically different microstructures.

The microstructures of the two films grown on the Te and As treated Si(111) substrates are shown in Fig. 1, demonstrating the different structural features. The film grown on the Te treated substrate has a very faulted microstructure, containing different twin grains, planar defects, and threading dislocations at the interface as well as through the whole film [Fig. 1(a)]. Furthermore, the polarity of the film is determined to be (111)A from convergent beam electron diffraction (CBED) [Fig. 1(b)] as well as from RHEED. The film-substrate interface is very rough, with about 15 nm modulations into the Si substrate due to the Te flux reacting with Si during cooling [Fig. 1(c)].

A very different quality of film is observed for growth on the As-passivated substrate [Fig. 1(d)]. Apart from the few wide lamella microtwins confined to the 0.8 μm region close to the interface and a few threading dislocations, the epilayer is single crystal with excellent structural quality over large areas. Double crystal x-ray rocking curves from the CdTe(333) reflection using Cu $K\alpha_1$ and a Si(133) crystal monochromater have a full width at half maximum of 87 arcs for a 5-μm-thick layer. The selected area diffraction pattern from the CdTe/Si interface shows the perfect align-

[a]Also at Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831; electronic mail: yanxin@uic.edu
[b]Also at Facultes Universitaires Notre-Dame de La Paix, Laborotoire L.I.S.E., Belgium.

 © 1999 American Institute of Physics
Downloaded 12 Mar 2002 to 128.219.47.178. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

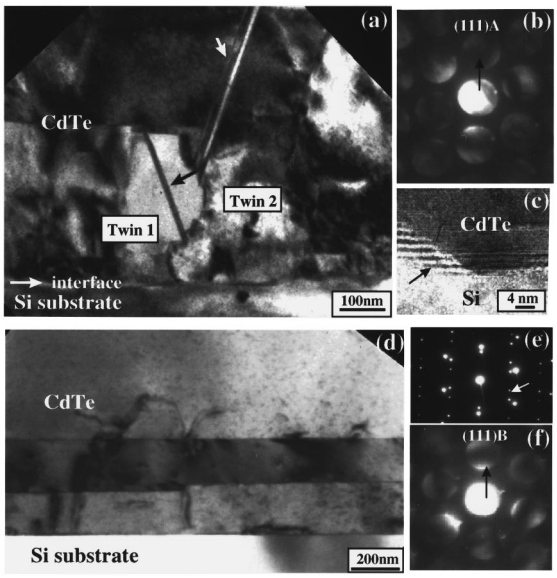

FIG. 1. (a) Low-magnification bright-field TEM image showing a cross-sectional view (in the [$\bar{1}10$] direction) of the sample grown on Te treated Si(111) substrate. (b) A CBED pattern shows the film has the (111)A polarity. (c) TEM image showing the roughness of film/substrate interface of Te treated sample. (d) Low-magnification bright-field TEM image showing a cross-sectional view (in the [$\bar{1}10$] direction) of the sample grown on the As passivated Si(111) substrate. (e) Selected area diffraction pattern shows the alignment of the epilayer with the substrate, one of the spots due to the lamellae twin is arrowed. (f) CBED pattern shows the film has the (111)B polarity.

ment of the CdTe(111) layer relative to the Si(111) substrate [Fig. 1(e)]. The polarity of the film is confirmed to be (111)B by CBED [Fig. 1(f)] and RHEED.

The difference in the quality of the films therefore appears to be related to the difference in the initial flux treatment of the Si(111) surface. Examining the CdTe/Si interface by energy dispersive x-ray spectroscopy in the TEM shows that the As that is initially deposited on the Si surface remains there for the subsequent growth of the CdTe film (Fig. 2). The three spectra show that only when the 1 nm probe is placed at the interface is there an As signal present (the two other spectra are obtained ~5 nm from the interface). Furthermore, quantitative analysis of the spectra gives an estimate of the As concentration as close to one atomic monolayer. These results are consistent with the *in situ* RHEED observations before initiation of the CdTe growth, and confirmed by x-ray photoemission spectroscopy.[13] The atomic structure of the interface of the CdTe(111)B/Si(111):As was examined using atomic resolution *Z*-contrast imaging. Figure 3(a) is an atomic resolution *Z*-contrast image (Fourier filtered) of the CdTe/Si interface with superimposed sketch of the atomic configuration. The elongated white spots in the image are atomic columns. From the raw image (not shown here) the first CdTe layer can be easily ascertained by the intensity difference at the interface, as CdTe has a higher atomic number than Si or As. The extra plane of the misfit dislocation is indicated. By drawing a Burgers circuit around the core, the edge component of the Burgers vector is 1/4[$11\bar{2}$], which is parallel to the interface, providing the explanation as to why there is no tilt of the epilayer with respect to the substrate. The average spacing between misfit dislocations is 1.9 nm. These are the grown-in misfit

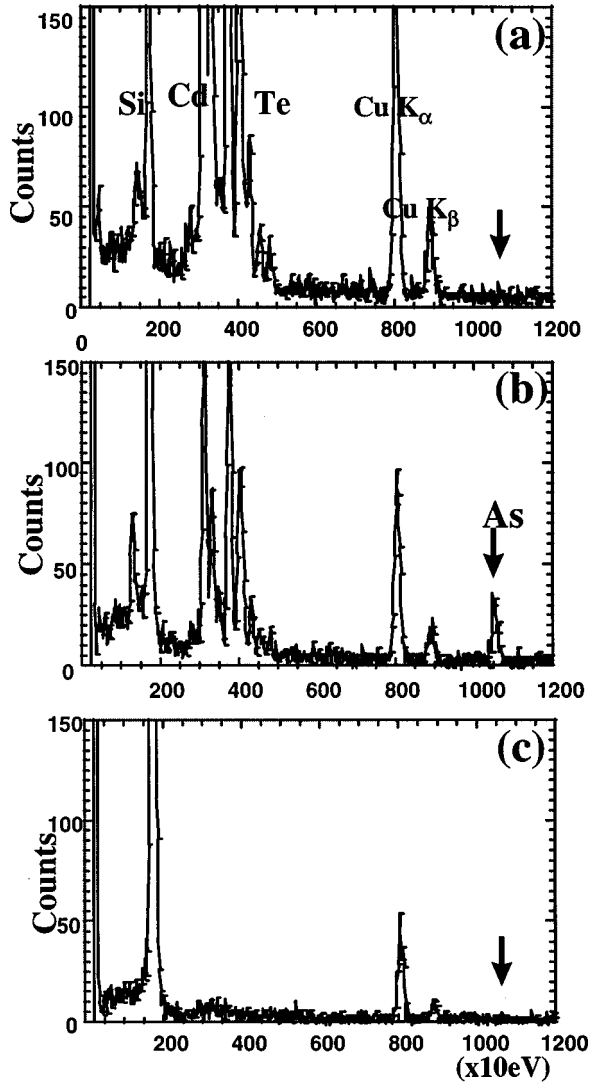

FIG. 2. Energy dispersive x-ray spectra from the As-passivated sample of (a) CdTe layer; (b) CdTe/Si interface; (c) Si substrate, confirming the presence of As at the interface. Cu signal is artifact due to spurious x-ray.

dislocations that have relieved the majority of the mismatch strain. *Z*-contrast image [Fig. 3(b)] from different areas along the same interface, shows that the first few layers of CdTe can also be deposited in a twinning position relative to the substrate. This indicates that CdTe can initially nucleate in two orientations with a twinning relationship, as shown schematically in Figs. 3(c) and 3(d). This means the film adopts either the substrate orientation with ABCABC‖ABC……, or in a twinning position to the substrate with ABCABC‖BACBAC.., where A, B, or C denotes the atomic double layer. It must be pointed out from the TEM observations that no islands or grains other than the few coherent twin boundaries are found in the region at the interface, where the twinned domains are of small quantity, and the film/substrate interface is atomically flat.

Based upon the above investigations, a mechanism for the direct growth of CdTe(111) on Si(111) substrates with either As or Te treatment is proposed. For the films grown on Te treated substrate, the substrate surface has been heavily modified by the Te flux during cooling, resulting in a very rough surface for the subsequent growth of the CdTe film. CdTe is initiated with island growth, and due to the rough

Downloaded 12 Mar 2002 to 128.219.47.178. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

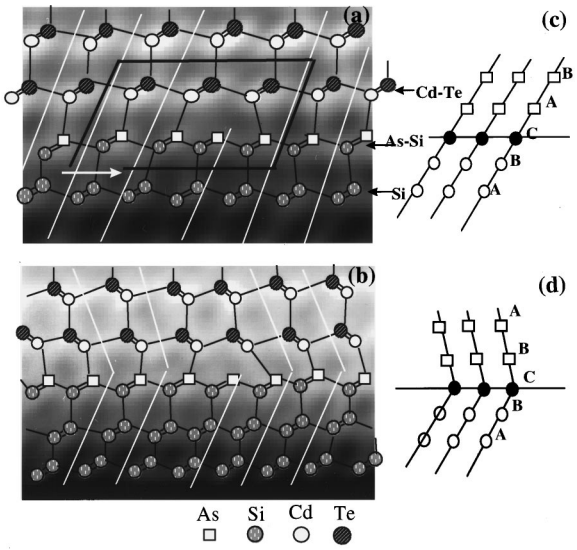

FIG. 3. (a) An atomic resolution *Z*-contrast image (Fourier filtered) of the As-passivated CdTe/Si interface viewed along the [110] direction. The sketch of the atomic configuration is superimposed on the image. The Burgers circuit drawn around the misfit dislocation is also shown. (b) Atomic resolution *Z*-contrast image (Fourier filtered) of a different region along the interface showing the twin oriented domain. Again the atomic configuration is schematically superimposed. (c) and (d) sketches showing the stacking sequence across the interface of the two possible epilayer orientations: corresponding to (a) and (b), respectively, (A, B, and C denote a double atomic layer).

substrate surface, Cd and Te adatoms would be expected to have short diffusion lengths on the surface, which results in the many twin grains at the interface. The remainder of the structural features that degrade the crystalline quality is the result of the growth of a CdTe(111)A film without an extra Cd flux.[14]

As shown by the above experimental observations, As is important in obtaining desired high-quality (111)B film. There are two main factors that result in the growth of single-domain epitaxial CdTe(111)B with high crystalline quality on Si(111); the As-passivated Si(111) surface which results in the (111)B polarity and the nature of atomic steps and terraces on the nominal Si(111) surface which give rise to layer growth free of multidomains.[12] It is well known that As replaces the outermost Si atoms of the double layer during passivation of the Si(111) surface in the MBE growth process,[15] and it is known from the earlier investigations that As stays there after the growth. Both imply that As is present at the interface as a monolayer separating CdTe and Si during the growth. Based on the As–Cd, As–Te bond formation energies,[16] it is likely that Cd is favored as the first atomic layer forming bond with the As at the interface, where the bonding configuration proceeds in a fashion such as Si–As–Cd–Te across the interface as shown in Fig. 3.

Even though it is known from the growth that Cd atoms have a very low sticking coefficient and would re-evaporate from the surface under only a Cd flux, the resultant CdTe(111)B layer growth implies that the presence of Te atoms supplied by stoichiometric flux is sufficient to stabilize the Cd on the surface. This occurs through a transition layer at the growth front. CdTe is initiated with Cd atoms forming one bond with As and three bonds with Te, producing a Te stabilized growth surface, which finally results in (111)B growth. Because of the high interfacial energy associated with the large lattice mismatch between CdTe and Si and the requirement of low temperature initiation, layer deposition starts with island nucleation. CdTe nucleation could initiate both at step edges and on the terraces, and because the atomic structures of the Si(111) surface comprise double layer steps giving the same atomic configuration from terrace to terrace, all the nuclei would have only two possible positions, i.e., the twining positions. In this system, the associated lattice mismatch energy is the same for the two possible depositions. However, the nuclei at twinning positions might have a higher interfacial energy due to the ''faulted'' stacking sequence across the interface, and therefore the majority of the nuclei would adopt the orientation of the substrate (as is observed experimentally). Growth then proceeds in a layer by layer fashion after several tens of monolayers have been deposited and the substrate temperature is raised to normal growth temperature. Because there is no tilt between the nucleating islands, the coherent double positioning boundaries are easily eliminated after a short nucleation stage.

In conclusion, we have shown that As passivation of a Si(111) substrate can have a dramatic effect on the quality of CdTe films grown by MBE. In particular, this passivation allows the direct growth of single crystal CdTe(111)B films on Si(111) substrates without the need for a buffer layer.

The project is funded through NSF DMR 9601792 and DMR 9733895 and by Lockheed Martin Energy Research Corporation, and is partially supported by Army Research Laboratory under Contract No. ARMY 97-2-0155 and Air Force Research Laboratory subcontracted through EPIR Ltd. under Contract No. F29601-98-C-0053, also with the Office of Naval Research under Contract No. N00014-98-1-0763. Y.X. wishes to thank G. Brill for help with the MBE growth. R. S. acknowledges support from the Belgian Fund for Scientific Research.

[1] R. Sporken, M. D. Lange, C. Masset, and J. P. Faurie, Appl. Phys. Lett. **57**, 1449 (1990).
[2] N. K. Dhar, M. Zandian, J. G. Pasko, J. M. Arias, and J. H. Dinan, Appl. Phys. Lett. **70**, 1730 (1997).
[3] S. Sivananthan, X. Chu, J. Reno, and J. P. Faurie, J. Appl. Phys. **60**, 1359 (1986).
[4] P. Boiuer and R. Sporken (private communications).
[5] R. Sporken, Y. P. Chen, S. Sivananthan, M. D. Lange, and J. P. Faurie, J. Vac. Sci. Technol. B **10**, 1405 (1992).
[6] Y. P. Chen, J. P. Faurie, and S. Sivananthan, J. Electron. Mater. **24**, 475 (1995).
[7] H. Ebe and Y. Nishijima, Appl. Phys. Lett. **67**, 3138 (1995).
[8] R. Sporken, F. Malengreau, Y. P. Chen, T. van Gemmeren, J. Ghijsen, and S. Sivananthan, Phys. Mag. **18**, 21 (1996).
[9] H. Zogg and S. Blunier, Appl. Phys. Lett. **49**, 1531 (1986).
[10] R. Korenstein, P. Madison, and P. Hallock, J. Vac. Sci. Technol. B **10**, 1370 (1991).
[11] Y. Xin, N. D. Browning, S. Rujirawat, S. Sivananthan, Y. P. Chen, P. D. Nellist, and S. J. Pennycook, J. Appl. Phys. **84**, 4292 (1998).
[12] S. Rujirawat, Y. Xin, N. D. Browning, S. Sivananthan, D. J. Smith, Y. P. Chen, and V. Nathan, Appl. Phys. Lett. **74**, 2346 (1999).
[13] R. Sporken, P. Boieriu, F. Wiame, S. Rujirawat, Y. Xin, M. Djendinov, N. D. Browning, and S. Sivananthan (unpublished).
[14] S. Rujirawat and R. Sporken (unpublished).
[15] R. D. Bringans, CRC Crit. Rev. Solid State Mater. Sci. **17**, 353 (1992).
[16] Landolt-Bornstein, in *Numerical Data and Functional Relationships in Science and Technology*, Semiconductors, Vol. 17, edited by K.-H. Hellwege (Springer, Berlin, 1982).

Downloaded 12 Mar 2002 to 128.219.47.178. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp