Oxygen on the (100) CdTe surface

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We have investigated oxygen on CdTe substrates by means of x-ray photoelectron spectroscopy (XPS) and reflection high-energy electron diffraction (RHEED). A Te oxide layer that was at least 15 Å thick was found on the surface of as-delivered CdTe substrates that were mechanically polished. This oxide is not easily evaporated at temperatures lower than 350 °C. Furthermore, heating in air, which further oxidizes the CdTe layer, should be avoided. Etching with HCl acid (15% HCl) for at least 20 s and then rinsing with de-ionized water reduces the Te oxide layer on the surface down to 4% of a monoatomic layer. However, according to XPS measurements of the O 1*s* peak, 20%–30% of a monoatomic layer of oxygen remains on the surface, which can be eliminated by heating at temperatures ranging between 300 and 340 °C. The RHEED patterns for a molecular beam epitaxially (MBE)-grown CdTe film on a (100) CdTe substrate with approximately one monoatomic layer of oxidized Te on the surface lose the characteristics of the normal RHEED patterns for a MBE-grown CdTe film on an oxygen-free CdTe substrate.

I. INTRODUCTION

The potential applications of CdTe in the areas of optoelectronics and solar energy conversion, and as a substrate for commercially important HgCdTe materials have given rise to considerable attention to the growth of high-quality CdTe. The difficulty to reproducibly grow and dope CdTe, however, limits its technological and commercial exploitation. Thus, it is essential at the present to find and eliminate any contamination that may result in a deterioration of molecular beam epitaxially (MBE)-grown samples.

Several articles have reported on heat treatment of CdTe[1,2] and $Cd_{0.96}Zn_{0.04}Te$ substrates in ultrahigh vacuum prior to the MBE growth of CdTe.[3] In addition, a number of workers have studied CdTe surfaces resulting from various surface treatments using Auger electron spectroscopy, x-ray photoelectron spectroscopy (XPS), and photoluminescence techniques.[4–9] But nobody has reported on the effect of oxide on the MBE growth of CdTe. As is well known, heating GaAs at 400 and 580 °C can completely eliminate small amounts of carbon[10] and much larger amounts of oxygen,[11] respectively. Therefore, many groups oxidize GaAs substrates with H_2SO_4 plus H_2O and H_2O_2 or even by heating the substrate in air at temperatures ranging from 160 to 250 °C in order to reduce carbon contamination on the surface. This procedure results in the growth of good quality GaAs epilayers and related compounds. Naturally, one could attempt to use a similar technique in the heat treatment of CdTe substrates, i.e., oxidize the CdTe in order to prevent carbon contamination of the surface, which is not easily removed as reported by Shaw *et al.*[2] and Wu *et al.*[3] In order to determine if such a technique is applicable to CdTe, it is essential to investigate the effect of oxygen on the CdTe surface. In this article we report on some experimental results on the oxidized CdTe (100) surface.

II. EXPERIMENTAL DETAILS

The mechanically polished (100) CdTe substrates employed in this work were treated according to the following procedure unless stated otherwise. They were first cleaned with methanol, acetone, and trichlorethylene (or chloroform). This is our standard cleaning procedure. The substrates were then chemomechanically polished with a methanol, ethylenglycol and bromine (125:75:2) solution for several minutes and rinsed in methanol. In order to be chemomechanically polished, the substrates were attached to a holder with wax that required a temperature of about 80 °C for several minutes. This procedure, which involves the use of wax, introduces additional contamination that was removed with the cleaning procedure described above. Immediately prior to loading the substrates into the high vacuum transfer system, they were rinsed in de-ionized water, briefly dipped in hydrochloric acid (15% HCl) for 30 s and then rinsed in de-ionized water. The elapsed time until the substrate was loaded into the transfer system was kept as short as possible; about three minutes. The substrate was maintained in ultrahigh vacuum for about 10 h before heat treatment. The growth chamber and the XPS chamber are connected by means of a transfer system, whose vacuum was normally better than 2×10^{-9} Torr, enabling *in situ* observations of reflection high-energy electron diffraction (RHEED) patterns in the growth chamber as well as *in situ* XPS measurements before, during, and after heat treatment. XPS measurements were conducted with a Riber MAC2 electron spectrometer using both $MgK\alpha(h\nu=1253.6$ eV) and $AlK\alpha(h\nu=1486.6$ eV) x-ray sources without a monochromator and with a filament current of 10 mA and a voltage of 10 kV. The background vacuum of the XPS chamber was normally better than 4×10^{-10} Torr during XPS measurements. The substrates were heated at various temperatures in either the transfer system or the MBE growth chamber. The temperature of the molybdenum substrate holder was measured with an

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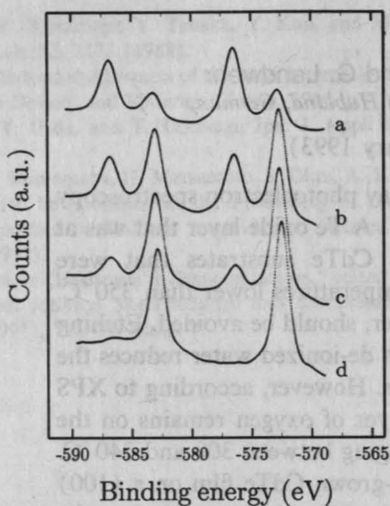

FIG. 1. Photoelectron intensities of the Te 3*d* peaks a) before heating and after heating b) at 300 °C, c) 350 °C, and d) 370 °C for 15 min. A Mg*Kα* x-ray source was used for the XPS measurements.

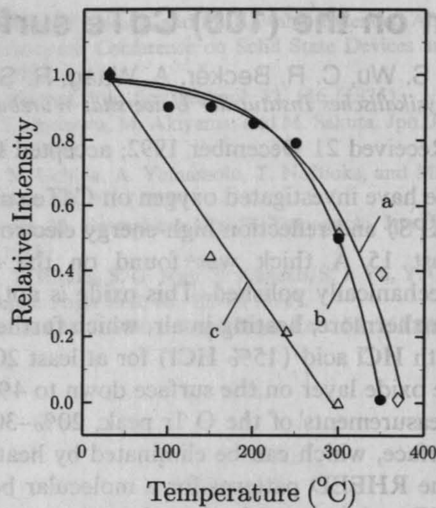

FIG. 2. Photoelectron intensities of the O 1*s* peak as a function of the heat treatment temperature in vacuum for a substrate that was a) cleaned but otherwise untreated, b) cleaned and polished according to Ref. 1, and c) cleaned, polished, and then etched with HCl acid (15% HCl) for 30 s according to Ref. 3. Curves a and b are least square fits of an exponential function to the experimental data, and curve c is a least square fit of a linear function.

accuracy of ±2 °C, by means of a thermocouple that was in physical contact with the substrate holder. The thermocouple was calibrated at the melting point of indium.

III. RESULTS AND DISCUSSION

The oxidized surface of a CdTe substrate, which had been neither chemomechanically polished nor etched in a HCl solution to remove the original oxide, was initially investigated. This mechanically polished, mirror-like (100) CdTe substrate was only cleaned as described above. An XPS spectrum of this sample in the vicinity of the Te $3d_{3/2}$ and Te $3d_{5/2}$ peaks is shown in Fig. 1(a). The peak due to the Te $3d_{3/2}$ core level is at 582.90 eV and the corresponding chemically shifted peak due to some form of Te oxide is at 586.56 eV. The amplitudes of the chemically shifted peaks are larger than that of the unshifted peaks as shown in Fig. 1(a). According to the calculations below, a surface layer that contains oxidized Te is at least 17 Å thick. Therefore, at least the first 5 monolayers contain Te oxide if a CdTe substrate is held in air for an extended period of time. The curves in Figs. 1(b)–1(d) show both the shifted and unshifted Te 3*d* peaks after heat treatment at 300, 350, and 370 °C in ultrahigh vacuum for 15 min, respectively. The chemically shifted Te 3*d* peak is still observable even after being heated at 370 °C.

The relative intensity (area) of the oxygen 1*s* peak for this substrate is plotted versus the temperature of the heat treatment in Fig. 2. Curve a is a least square fit of an exponential function to the experimental data. Waag *et al.* investigated oxygen contamination on CdTe substrates that had been cleaned, subsequently etched with a solution of bromine in methanol, and finally rinsed with methanol. The corresponding 1*s* intensities are reproduced in Fig. 2. Similarly, curve b is a least square fit of an exponential function to these experimental data. As can be seen, these two sets of data are very similar. This is in contrast to the data represented by curve c, which is a least square fit of a linear function. These heat treatment data are for a $Cd_{0.96}Zn_{0.04}Te$ substrate from Wu *et al.*,[3] which had been cleaned, polished in a solution of bromine in methanol, and then etched in a HCl solution as described above. Obviously, etching with HCl greatly facilitates the removal of oxygen from the surface and lowers the temperature necessary to completely remove oxygen from the surface. This is desirable because heating at temperatures higher than 350 °C will degrade a CdTe substrate according to Shaw *et al.*[2]

Oxygen contamination on the surface is detrimental to the MBE growth of CdTe. We have attempted to grow CdTe on a (100) CdTe substrate with approximately one monoatomic layer of oxidized Te on the surface as judged by the intensity of the chemically shifted Te $3d_{3/2}$ core level peak. After heating at 300 °C for 10 min, the RHEED patterns still consisted of streaks but they were less intense than those for a CdTe with no oxygen on the surface. However, no rings and no spots were present. When we grew CdTe on this surface, the RHEED patterns did not become brighter. In addition, they became spotty and then off angle streaks appeared, that is they lost the characteristics of the normal RHEED patterns for a CdTe film. This might be due to either oxygen or oxidized Te on the surface. Of course, after the cleaning, polishing, and etching procedure described above, no measurable oxidized Te is left on the surface. However, heating at a lower temperature or heating for a shorter period of time in order to keep the RHEED pattern smooth could leave some oxidized Te on the surface, and considerably affect the CdTe film quality.

This problem can be avoided if the sample is not heated in air after polishing and, if after etching with HCl acid and rinsing with de-ionized water, it is not exposed to air for appreciably longer than 10 min. We have measured the XPS peaks due to the Te 3*d* and O 1*s* core levels for

TABLE I. Thickness of Te oxide as calculated according to Eqs. (1)–(3) before and after various substrate treatments. Substrates 1–3 are as-delivered CdTe substrates that had been mechanically polished. Substrate 4 had been stored in air for one month after being etched in HCl (15%) for 20 s. Finally, substrate 5 is a molecular beam epitaxially grown layer on a CdTe substrate that had been exposed to air for one month.

Treatment	Subr. 1	Subr. 2	Subr. 3	Subr. 4	Subr. 5
No HCl etch	17.0±2 Å	16.7±2 Å	15.0 ±2 Å	9.0 ±1 Å	11.0 ±1 Å
HCl (15%) etch for 5 s	1.6±0.2 Å			0.02±0.02 Å	0.02±0.02 Å
HCl (15%) etch for 10 s		0.9±0.1 Å			
HCl (15%) etch for 20 s			0.06±0.03 Å		

CdTe substrates after our normal cleaning, polishing, and etching treatment and after heating in ultrahigh vacuum at temperatures ranging from 300 to 340 °C for 15 min. No oxygen contamination was found on the surface. This heat treatment is shown as a function of temperature for a $Cd_{0.96}Zn_{0.04}Te$ substrate in Fig. 2(c).[3]

An experiment to determine the influence of HCl on surface oxide was carried out on five CdTe substrates. All five substrates were mechanically polished. Three were as-delivered, one had been stored in air for one month after being etched in HCl (15%) for 20 s, and one whose surface was a MBE-grown CdTe layer had been stored in air for about one month at room temperature. These CdTe substrates were cleaned as described above and the original XPS amplitude of the chemically shifted Te $3d_{3/2}$ peaks was measured before etching with HCl (see Table I). This amplitude for the three as-delivered substrates differed by less than ±10%. The CdTe substrates were then etched with HCl acid (15%) for various periods of time and the XPS amplitude of the chemically shifted Te $3d_{3/2}$ peaks was measured and the results are listed in Table I. Figure 3 displays the resulting XPS peaks for the Te $3d_{3/2}$ core levels and the corresponding chemically shifted core levels due to oxygen for the three as-delivered substrates for different HCl etch time periods.

In order to determine how much oxide is left on the surface after etching with HCl acid for different periods of time, we have measured the Te 3*d*, Cd 3*d*, and O 1*s* core levels with XPS. The Cd 3*d* peak is chemically shifted only 0.8 eV by oxygen, according to Wagner *et al.*[12] This cannot be resolved, therefore, the Cd 3*d* peak for an oxidized CdTe surface containing oxidized Cd is wider than that for a clean CdTe surface. Furthermore, the Cd $M_5N_{45}N_{45}$ Auger peak is shifted and deformed by the presence of oxide. Comparing Cd 3*d* and Auger peaks one could qualitatively determine if some form of Cd oxide is on the surface but could not quantitatively determine the amount of Cd oxide. In contrast, the Te 3*d* peaks are chemically shifted to higher binding energies by about 3.66 eV. Thus, one can qualitatively determine the Te oxide on the surface. This is expressed as the ratio of the XPS intensity (amplitude) for the chemically shifted Te $3d_{3/2}$ peak to the total intensity of the Te $3d_{3/2}$ peaks, i.e., the sum of the amplitudes for the shifted and the unshifted Te $3d_{3/2}$ peaks. This ratio for Te oxide to total Te is shown as a function of time etched with HCl acid (15% HCl) in Fig. 4, curve a. Moreover, the amplitude of the peak due to the oxygen 1*s* core level was determined as a function of HCl time etched and is shown as curve b in Fig. 4.

If one assumes that all the Te in a layer of thickness *d* is oxidized, then according to XPS theory, the intensity due to the photoelectrons from the chemically shifted Te $3d_{3/2}$ core level is

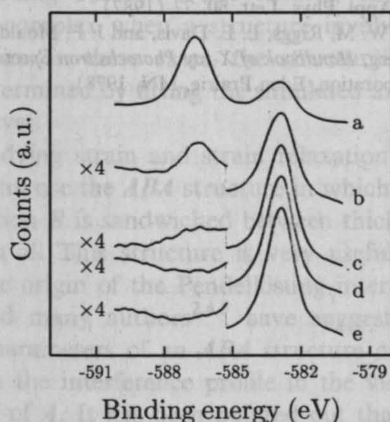

FIG. 3. Photoelectron measurements of the chemically shifted and unshifted Te $3d_{3/2}$ peaks of a substrate after being etched in HCl (15%) for a) zero seconds, b) 5 s, c) 10 s, and d) 20 s, as well as e) after growth of a CdTe film with a Te stabilized surface, by means of a Mg*Kα* x-ray source.

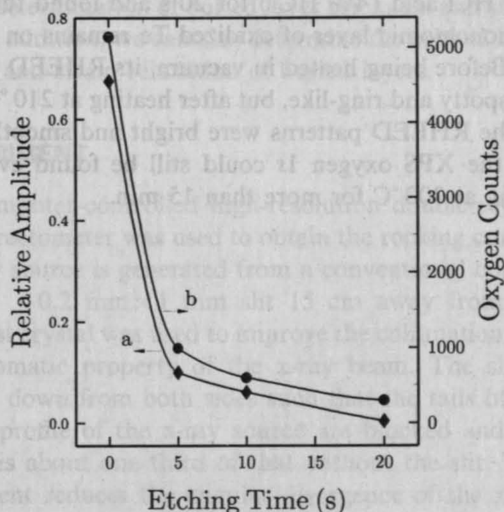

FIG. 4. Curve a shows the ratio of the XPS intensity (amplitude) for the chemically shifted Te $3d_{3/2}$ peak to the total intensity of the Te $3d_{3/2}$ peaks, i.e., the sum of the amplitudes for the shifted and the unshifted Te $3d_{3/2}$ peaks as a function of the HCl (15%) etch time. Similarly, curve b displays the photoelectron intensity of the O 1*s* peak as a function of HCl (15%) etch time.

$$I_0=I_{0\infty}\left[1-\exp\left(-\frac{d}{\lambda}\right)\right], \quad (1)$$

where $I_{0\infty}$ is the intensity from a thick oxidized film and λ is the photoelectron escape depth. Furthermore, if the Te below this layer is not oxidized, then the intensity due to the photoelectrons from the unshifted Te $3d_{3/2}$ core level is

$$I_T=I_{T\infty}\exp\left(-\frac{d}{\lambda}\right), \quad (2)$$

where $I_{T\infty}$ is the intensity from a thick film on the surface that is not oxidized. The escape depth of the Te $3d_{3/2}$ photoelectrons excited by Mg$K\alpha$ x ray can be calculated to be 15 Å by means of the energy dependence relationship $\lambda \sim E^{0.75}$ according to Wagner *et al.*[12] Finally, because both $I_{0\infty}$ and $I_{T\infty}$ are due to the Te $3d_{3/2}$ core level, even though $I_{0\infty}$ is chemically shifted, we assume that these two quantities are equal. This results in

$$d=\lambda \ln\left(\frac{I_0}{I_T}+1\right). \quad (3)$$

Using this formula, the thicknesses of the Te oxide layer for different etch times were estimated and are listed in Table I. It is readily apparent that etching CdTe substrates with HCl acid (15% HCl) for 20 s can almost completely eliminate Te oxide.

The oxygen contamination on the surface after etching with HCl has also been determined from the XPS peak due to the oxygen 1*s* core level. The results are shown as curve b in Fig. 4. Using our published method,[1,3] we have calculated that a layer of oxygen with the approximate thickness of 0.3–0.5 Å is left on the surface after etching with HCl (15%) for 20 s. According to the results above, this layer of oxygen is not in the form of Te oxide.

As might be expected, etching CdTe with more dilute HCl acid requires a longer etch time in order to obtain an oxygen free surface. We have etched a CdTe substrate with dilute HCl acid (4% HCl) for 20 s and found that about one monoatomic layer of oxidized Te remains on the surface. Before being heated in vacuum, its RHEED patterns were spotty and ring-like, but after heating at 210 °C for 15 min the RHEED patterns were bright and smooth. However, the XPS oxygen 1*s* could still be found even after heating at 300 °C for more than 15 min.

IV. CONCLUSIONS

In conclusion, CdTe substrates are oxidized when stored in air. The Te oxide layer on the surface can be 15 Å or thicker even if the substrate is not heated in air. This oxide on CdTe is not easily evaporated at temperatures lower than 350 °C. Therefore, heating in air which further oxidizes the CdTe layer should be avoided. Etching with HCl acid (15% HCl) for at least 20 s and then rinsing with de-ionized water almost completely removes the Te oxide layer on the surface. However approximately 20%–30% of a monoatomic layer of oxygen remains on the surface as determined from the O 1*s* peak. This can be eliminated by heating at temperatures ranging between 300 and 340 °C.

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[1] A. Waag, Y. S. Wu, R. N. Bicknell-Tassius, and G. Landwehr, Appl. Phys. Lett. **54**, 2662 (1989).
[2] J. L. Shaw, L. J. Brillson, S. Sivananthan, and J. P. Faurie, Appl. Phys. Lett. **56**, 1266 (1990).
[3] Y. S. Wu, C. R. Becker, A. Waag, R. N. Bicknell-Tassius, and G. Landwehr, Appl. Phys. Lett. **60**, 1878 (1992).
[4] U. Solzbach and H. J. Richter, Surf. Sci. **97**, 191 (1980).
[5] J.-P. Häring, J. G. Werthen, R. H. Bube, L. Gulbrandsen, W. Jansen, and P. Luscher, J. Vac. Sci. Technol. A **1**, 1469 (1983).
[6] A. J. Ricco, H. S. White, and M. S. Wrighton, J. Vac. Sci. Technol. A **2**, 910 (1984).
[7] R. D. Feldman, R. L. Opila, and P. M. Bridenbaugh, J. Vac. Sci. Technol. A **3**, 1988 (1985).
[8] Y.-C. Lu, C. M. Stahle, R. S. Feigelson, and J. Morimoto, J. Appl. Phys. **62**, 4453 (1987); Y.-C. Lu, R. S. Feigelson, and R. K. Route, J. Appl. Phys. **67**, 2583 (1990).
[9] Z. Sobiesierski, I. M. Dharmadasa, and R. H. Williams, Appl. Phys. Lett. **53**, 2623 (1988).
[10] A. Saletes, J. Massies, and J. P. Contour, Jpn. J. Appl. Phys. **25**, L48 (1986).
[11] A. J. SpringThorpe, S. J. Ingrey, B. Emmerstorfer, P. Mandeville, and W. T. Moore, Appl. Phys. Lett. **50**, 77 (1987).
[12] C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, edited by G. E. Mullenberg, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin Elmer Corporation, Eden Prairie, MN, 1978).