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# Removal of oxygen and reduction of carbon contamination on (100) $Cd_{0.96}Zn_{0.04}Te$ substrates

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**Abstract.** X-ray photoelectron and Auger electron spectroscopy as well as *reflection high energy electron diffraction* have been used to investigate the influence of heat treatment and sputtering on the oxygen and carbon contamination of the (100) $Cd_{0.96}Zn_{0.04}Te$ surface. It was found that oxygen contamination can be completely eliminated from the surface at 300 °C in an ultra-high vacuum but not carbon. Heating at still higher temperatures decreases the carbon contamination only slightly while increasing the Zn to Cd ratio on the surface considerably. This affects the $Cd_{0.96}Zn_{0.04}Te$ surface structure and hence subsequent molecular beam epitaxial growth. We have found that sputtering with argon ions at an incident angle ranging between 20° and 60° at temperatures between 200 and 250 °C can remove nearly all carbon contamination from the surface without destroying the (2 × 1) surface reconstruction.

## 1. Introduction

$Cd_{1-x}Zn_xTe$ (CdZnTe) has various advantages as a substrate for infrared detectors containing either HgCdTe or HgZnTe. Most importantly, the lattice constant can be varied between 6.102 Å for ZnTe and 6.481 Å for CdTe, and hence can be matched to both HgCdTe and HgZnTe alloys [1, 2]. Surface treatment is very important for both device processing [3, 4] and molecular beam epitaxial (MBE) growth [5–7]. A number of workers have studied the surface of CdTe substrates with various analytical tools, such as x-ray photoelectron spectroscopy (XPS) [5] and Auger electron spectroscopy (AES) [6, 7]. Thermal effects on CdZnTe substrates have recently been reported on by Wu *et al* [8].

The usual surface preparation for substrates is mechanical polishing followed by chemical etching or chemo-mechanical polishing and then etching, normally with dilute HCl or a solution of bromine in methanol. In these processes, bromine and an inorganic acid are usually involved, leaving the surface depleted in Cd [5, 7] and contaminated by impurities such as bromine and chlorine. Furthermore the surface is exposed to the atmosphere briefly before the substrate can be loaded into the ultra-high vacuum chamber. This results in further contamination by oxygen and carbon. The problem is how to eliminate these contaminants from the substrate surface. In this paper we briefly report on a method for eliminating or reducing these contaminants on $Cd_{0.96}Zn_{0.04}Te$ substrate surfaces.

## 2. Experimental details

The (100) $Cd_{0.96}Zn_{0.04}Te$ substrates were chemo-mechanically polished for several minutes, degreased using chloroform, acetone and methanol, etched in a weak bromine/methanol solution and rinsed in methanol. Immediately prior to loading the substrates into the high vacuum transfer system, they were rinsed in de-ionized water, dipped briefly in hydrochloric acid and then rinsed in de-ionized water so as to remove all of the original oxide and carbon from the substrate surface. We have found that the oxide formed during the last rinse in de-ionized water is more easily removed in subsequent steps than is the original oxide. The elapsed time before the substrate was transferred into the transfer system was kept as short as possible (about three minutes). The substrate was maintained in an ultra-high vacuum for several hours before heat treatment.

The substrates were heat treated in either the surface analysis chamber or the MBE growth chamber. The growth chamber and the surface analysis chamber are connected by means of the transfer system, whose vacuum was normally better than $2 \times 10^{-9}$, enabling *in situ* observations of reflection high energy electron diffraction (RHEED) patterns in the growth chamber as well as *in situ* XPS and AES measurements before, during and after heat treatment. XPS and AES measurements were conducted with a Riber MAC2 electron spectrometer using both Mg $K_\alpha$ ($h\nu = 1253.6$ eV) and Al $K_\alpha$ ($h\nu = 1486.6$ eV) x-ray sources without a monochro-

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mator and with a filament current of 30 mA and a voltage of 10 kV. A detailed description has been given previously [5, 9]. The background vacuum in the surface analysis chamber was normaly better than $4\times10^{-10}$ Torr during the XPS or AES measurements. The surface analysis chamber also contained an ion gun which was used to sputter some of the substrates. The temperature of the molybdenum substrate holder was measured with an accuracy of ±2 °C, by means of a thermocouple which was in physical contact with the substrate holder and which was calibrated at the melting point of indium.

## 3. Results and discussion

Thermal effects on oxygen and carbon contamination on the surface are shown in figures 1 and 2. In this experiment the sample was heated in steps from low to high temperatures, stopping for 15 minutes at each temperature unless otherwise stated. Before heat treatment the concentration of carbon on the surface was more than three times larger than that of oxygen, according to the XPS measurements. As the substrate temperature was raised the concentrations of both the carbon and oxygen on the surface decreased. Heating the substrate at 300 °C for 15 minutes completely removed oxygen from the surface, as indicated by the XPS results depicted by curve (*d*) in figure 1. However, the almost unshifted carbon 1s peak at about 283.7 ± 0.6 eV was still significant at this temperature, as indicated in figure 2. In fact, it could not be completely eliminated at temperatures up to 340 °C. Using the attenuation of the Cd $3d_{3/2}$ core level peak due to the carbon on the surface, the carbon thickness after heating at 300 °C was determined to be about 0.2 Å, or about 10% of a monolayer [8, 10]. In addition the calibrated C 1s signal resulted in a carbon thickness of about 0.5 Å, or about 30% of a monolayer, which is within the experimental uncertainty of the first method. No bromine or chlorine surface contamination could be found after heat treatment by XPS.

In contrast, appreciable changes in the Zn surface concentration occur when the substrate is heated to temperatures higher than 300 °C, and lower temperatures also have a large influence on the surface structure. The ratio of the x-ray photoelectron amplitude of the Cd $3d_{3/2}$ core level to that of Te was about 0.40 at temperatures less than 200 °C, but was larger, a nearly constant 0.49, at temperatures ranging from 200 to 340 °C, as shown by curve (*a*) in figure 3. Here the experimental error was about 0.01. In contrast, the ratio of the relative amplitude of the Zn $L_3M_{45}M_{45}$ Auger peak to that of the Cd $3d_{3/2}$ core level peak was nearly constant in the temperature region between 200 and 300 °C, and increased sharply for temperatures greater than 300 °C, as indicated by curve (*b*) in figure 3. Here the background changed less than 1% . From curve (*b*) in figure 3 one can estimate that the Zn content increases by at least a factor of two between 300 and 340 °C. This obviously has a large effect on the surface stoichiometry of the CdZnTe substrate and cannot be neglected.

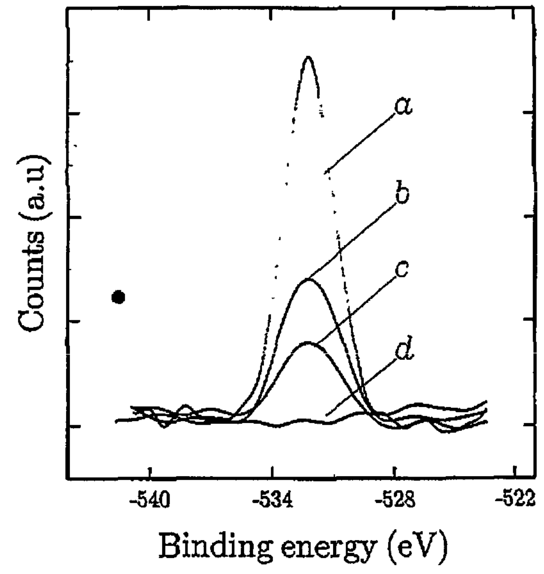

**Figure 1.** XPS spectra in the region of the oxygen 1s peak of a CdZnTe substrate after heat treatment at (*a*) 30 °C, (*b*) 150 °C, (*c*) 240 °C and (*d*) 300 °C using an Al $K_\alpha$ x-ray source.

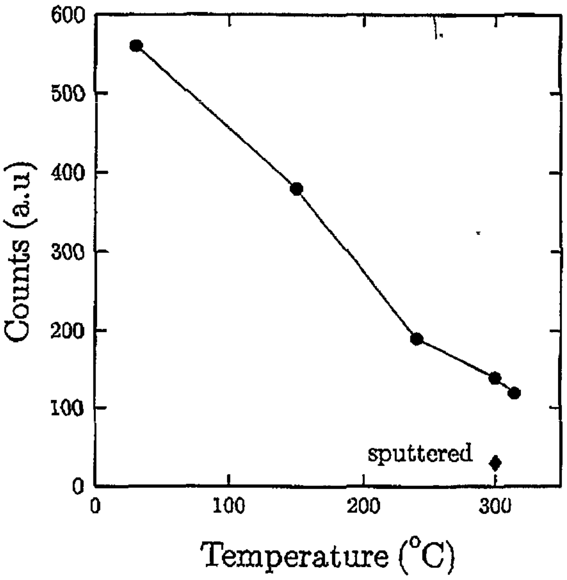

**Figure 2.** Photoelectron intensity of the carbon 1s peak as a function of heat treatment temperatures, with an Al $K_\alpha$ X-ray source. The diamond indicates the carbon 1s intensity after sputtering with Ar ions at 210 °C for 30 min.

Sputtering the CdZnTe substrate surface with Ar ions before the heat treatment described above results in a very rough surface. By sputtering the heat-treated substrate surface with Ar ions accelerated to 650 V at temperatures between 200 and 250 °C and at angles incident to the surface ranging from 20° to 60°, most but not all of the carbon could be removed without completely destroying the surface reconstruction. The photoelectron intensity of the carbon 1s peak of a CdZnTe substrate which was sputtered at 210 °C for 30 minutes with Ar is indicated by a diamond in figure 2.

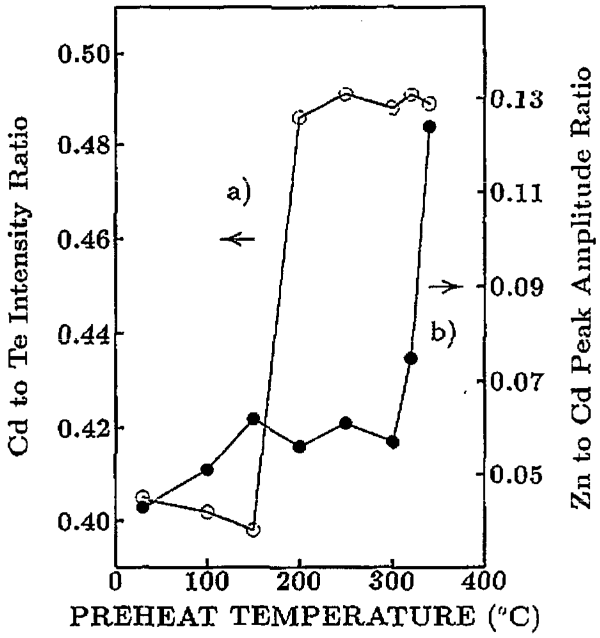

**Figure 3.** The intensity ratios of Cd to Te and Zn to Cd for a CdZnTe substrate versus heat treatment temperature, with a Mg $K_\alpha$ x-ray source: (*a*) The ratio of the XPS intensity of the Cd $3d_{3/2}$ core level to that of Te. (*b*) The ratio of the Zn $L_3M_{45}M_{45}$ amplitude to that of the Cd $3d_{3/2}$ core level. These amplitudes have been divided by the corresponding background signal.

The photoelectron intensity of the C 1s energy level was reduced by a factor of about five, which means that only about 2–6% of the lattice sites on the surface were occupied by carbon atoms.

We have also sputtered an MBE-grown CdTe film which was deliberately exposed to air for several minutes. The carbon concentration after exposure was approximately 30% of that of a CdZnTe substrate before heat treatment. This contamination could be completely removed by sputtering with the above experimental conditions without destroying the (2 x 1) reconstruction in the RHEED patterns.

Initial tests of MBE growth of CdTe on CdTe substrates that had been ion sputtered at normal incidence at room temperature resulted in poor structural quality CdTe, i.e. no RHEED patterns could be found. We also tried to anneal sputtered substrates for several hours at temperatures ranging between 300 and 350 °C, and found only a few bright spots in the RHEED pattern, which indicates that the surface was very rough. Lu *et al* [11] and Janowitz *et al* [12] oberved a clear low energy electron diffraction (LEED) pattern containing surface reconstruction after annealing ion-sputtered CdTe substrates, but to our knowledge no one has succeeded in the MBE growth of CdTe on a sputtered surface. This may be because the surface sputtered at normal incidence at room temperature is too rough for MBE growth. Investigations of the effect of Ar ion sputtering at different angles of incidence on the MBE growth on CdZnTe substrates are underway.

## 4. Conclusions

In conclusion, heating CdZnTe substrates at 300 °C in vacuum can completely eliminate oxygen contamination from the surface, but can only reduce carbon contamination on the surface to approximately 25% of the original value. In addition, heat treatment changes the surface stoichiometry, and at temperatures higher than 300 °C it could have adverse effects on the MBE growth of lattice-matched films. By sputtering the substrate surface with Ar ions accelerated to 650 V at temperatures between 200 and 250 °C and at angles incident to the surface ranging from 20° to 60°, nearly all of the carbon could be eliminated without destroying the (2 x 1) reconstruction on the surface.

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## References

[1] Myers T H *et al* 1989 *J. Vac. Sci. Technol.* A 7 300
[2] Sivananthan S, Lange M D, Monfroy G and Faurie J P 1988 *J. Vac. Sci. Technol.* B 6 788
[3] Ricco A J, White H S and Wrighton M S 1984 *J. Vac. Sci. Technol.* A 2 910
[4] Häring J-P, Werthen J G, Bube R H, Gulbrandsen L, Jansen W and Luscher P 1983 *J. Vac. Sci. Technol.* A 1 1469
[5] Waag A, Wu Y S, Bicknell-Tassius R N and Landwehr G 1989 *Appl. Phys. Lett.* 54 2662
[6] Feldman R D, Opila R L and Bridenbaugh P M 1985 *J. Vac. Sci. Technol.* A 3 1988
[7] Shaw J L, Brillson L J, Sivananthan S and Faurie J P 1990 *Appl. Phys. Lett.* 56 1266
[8] Wu Y S, Becker C R, Waag A, Bicknell-Tassius R N and Landwehr G 1992 *Appl. Phys. Lett.* 59 1266
[9] Wu Y S, Becker C R, Waag A, Bicknell-Tassius R N and Landwehr G 1991 *J. Appl. Phys.* 69 268
[10] Wagner C D, Riggs W M, Davis L E and Moulder J F 1978 *Handbook of X-ray Photoelectron Spectroscopy* ed G E Mullenberg (Eden Prairie, MN: Perkin Elmer)
Waldrop J R, Grant R W, Kowalczyk S P and Kraut E A 1985 *J. Vac. Sci. Technol.* A 3 835
[11] Lu Y C, Feigelson R S and Route R K 1990 *J. Appl. Phys.* 67 2583
[12] Janowitz C, Manzke R, Skibowski M and Orlowski B A 1991 *Surf. Sci.* 247 100