Thermal effects on (100) CdZnTe substrates as studied by x-ray photoelectron spectroscopy and reflection high energy electron diffraction

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The influence of different CdZnTe substrate treatments prior to II-VI molecular beam epitaxial growth on surface stoichiometry, oxygen, and carbon contamination has been studied using x-ray photoelectron spectroscopy and reflection high energy electron diffraction. Heating the substrate at 300 °C can eliminate oxygen contamination, but cannot completely remove carbon from the surface. Heating at higher temperatures decreases the carbon contamination only slightly, while increasing the Zn–Cd ratio on the surface considerably. The magnitude of the latter effect is surprising and is crucial when one is using lattice matched CdZnTe (Zn 4%) substrates.

CdZnTe is an important substrate for infrared detectors containing either HgCdTe or HgZnTe because it offers tunability of the lattice constant and band gap. The lattice constant varies from 6.102 Å for ZnTe to 6.481 Å for CdTe and can be lattice matched to HgCdTe or HgZnTe alloys.[1,2] Its band gap ranges from 2.3 to 1.6 eV, which is large enough to provide minority-carrier confinement in abrupt heterostructures, e.g., multiquantum wells, that are conveniently grown by molecular beam epitaxy (MBE).[3-5]

Surface treatment is very important for both device processing[6,7] and MBE growth.[8-10] A number of workers have recently studied the surface of CdTe substrates with various analytical tools, such as x-ray photoelectron spectroscopy (XPS)[8] and Auger electron spectroscopy.[9,10] However, to our knowledge no one has reported in detail on the preparation of CdZnTe substrates.

The usual surface preparation is mechanical polishing followed by chemical etching or chemomechanical polishing and then etching, normally with dilute HCl or bromine/methanol. In these processes, bromine and an inorganic acid is usually involved, leaving the surface depleted of Cd (Ref. 8) 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 ultrahigh vacuum chamber. This results in further contamination by oxygen and carbon. How does one treat this surface in order to obtain a clean and stoichiometric surface?

Dal'Bo *et al.*[11] and Lentz *et al.*[12] preferentially heat their CdZnTe substrates at 340 °C. In order to prevent degradation of the reflection of high energy electron diffraction (RHEED) pattern before growth, the substrate was subjected to a Cd or Te environment. Han *et al.* heat CdZnTe substrates at 300 °C for 10 min in order to drive off residual impurities and to insure a stoichiometric surface.[13]

As is well known, heating GaAs at 400 and 580 °C can completely eliminate carbon[14] and oxygen,[15] respectively. In contrast, to our knowledge nothing has been reported in the literature, concerning the temperatures at which carbon and oxygen are removed from the surface of CdZnTe substrates. In this investigation we have employed XPS

and RHEED in order to determine what effect heat treatment has on the CdZnTe surface in an ultrahigh vacuum.

The substrates we employed in this work were (100)CdZnTe (Zn 4%). They were chemomechanically polished for several minutes, degreased using standard solvents, 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 deionized water, briefly dipped in hydrochloric acid and then rinsed in deionized water so as to remove all of the original oxide and carbon from the substrate surface. The substrates were then mounted under normal atmospheric conditions on a molybdenum block using colloidal graphite. We have found that the oxide formed during the last deionized water rinse is more easily removed in the 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 ultrahigh vacuum for about 15 h before heat treatment.

The growth chamber and the XPS chamber are connected by means of the transfer system, whose vacuum was normally better than 2×10^{-9} enabling *in situ* observations of the RHEED pattern 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 without a monochromator. A detailed description has been given previously.[8,16] The substrates were usually heat treated in the MBE growth chamber and occasionally in the XPS chamber. Moving the substrate through the transfer system had no effect on the XPS results. The temperature of the molybdenum substrate holder was carefully calibrated at the melting point of indium.

By keeping the substrate at 230 ± 30 °C for several tens of minutes, one could observe an improvement in the RHEED patterns for smooth surfaces, i.e., broken streaks with weak half order reconstructions in the (011), (010), and (001) azimuths. In this letter we consistently use the convention of referring to the direction of the incident electrons when referring to reconstruction in a particular azimuth. After 10 min at 300 °C, the oxygen 1s peak in the

XPS spectrum completely disappeared, and the broken streaks in the RHEED patterns were brighter and still homogeneous. If a 40–60 Å thick CdTe buffer is grown at this temperature for half a minute with a CdTe flux of $3.0–3.5\times10^{-7}$ Torr, these streaks were no longer broken but much darker. The original brightness of the RHEED patterns is re-established if a thicker CdTe buffer is grown on the CdZnTe substrate at 300 °C. However with a thicker CdTe buffer the advantage of lattice matching to HgCdTe or HgZnTe is lost.

In general the RHEED patterns are appreciably worse at 340 °C as compared to 300 °C. The subsequent growth of CdTe is, however, much better at 340 °C as judged by the brightness of the RHEED patterns and the presence of Kikuchi lines. Some investigators[11,12] use either a Cd or Te environment in order to prevent degradation of the reflection of high energy electron diffraction (RHEED) pattern before growth. We have found the following procedure quite useful. The substrate is heated to 340 °C and CdTe is grown for merely a couple of seconds. The temperature is lowered to about 300 °C and then raised to 340 °C where CdTe is again grown for a couple of seconds. This is repeated several times depending upon the RHEED pattern which should be very bright with homogeneous streaks. The growth is continued for about 2 min while the temperature is lowered first to 270 °C and then to 230 °C.

A good RHEED pattern does not insure the absence of carbon from the surface. We have exposed a freshly grown CdTe film to atmosphere for 3 min and then heated it at 300 °C for 5 min. The carbon present corresponded to a layer with a thickness of about 0.5 Å according to XPS measurements of the C 1s peak described below. Nevertheless the RHEED patterns were good with clear half order reconstruction in the (001), (010), and (001) azimuths.

Thermal effects on oxygen and carbon contamination on the CdZnTe surface are shown in Fig. 1. In this experiment the sample was heated in 50 °C steps from low to high temperatures, stopping for 15 min at each temperature unless otherwise stated. Before heat treatment the carbon concentration on the surface was much larger than that of oxygen according to the XPS measurements as shown in Fig. 1, if one uses the atomic sensitivity factors for carbon and oxygen, 0.205 and 0.63, respectively, according to Ref. 17. As the substrate temperature was raised the concentration of both the carbon and oxygen on the surface was reduced. Heating the substrate at 300 °C for 15 min completely removed oxygen from the surface, as indicated by the XPS results depicted by curve a in Fig. 1. However the nearly unshifted carbon 1s peak at about 283.7±0.6 eV was still significant at this temperature as indicated in Fig. 2. In fact it could not be completely eliminated at temperatures up to 340 °C. This is consistent with the experiment of Shaw et al.[10] At these temperatures appreciable changes in the Zn surface concentration occur as discussed below.

According to XPS theory, the intensity of the photoelectrons from a film of thickness d, is
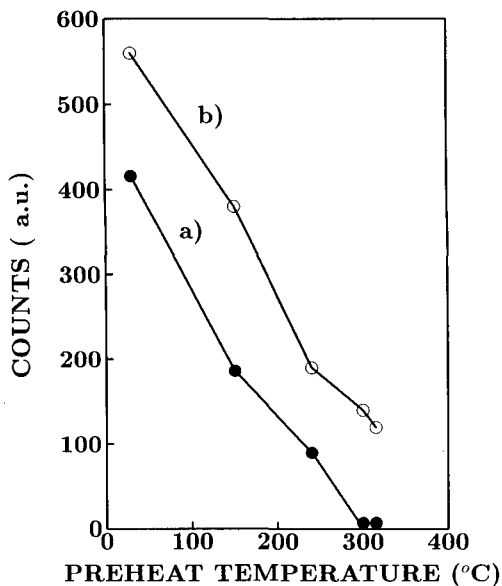

FIG. 1. Photoelectron intensities of (a) the oxygen 1s peak and (b) the carbon 1s peak as a function of heat treatment temperatures, with an Al $K\alpha$ x-ray source.

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

where I_∞ is the intensity from a thick film and λ is the photoelectron escape depth. The escape depth of the C 1s photoelectrons excited by Al $K\alpha$ x ray can be calculated to be 22 Å by means of the energy dependence relationship $\lambda \sim E^{0.75}$ according to Wagner et al.[17] In order to calibrate the XPS measurements of the C 1s peak we measured the C 1s peak of a thick graphite film on a Mo block. Using the above relationship and parameters we calculated that the carbon concentration on a substrate after heating at 300 °C corresponded to a thickness of about 0.5 Å or to about 30% of a monolayer.

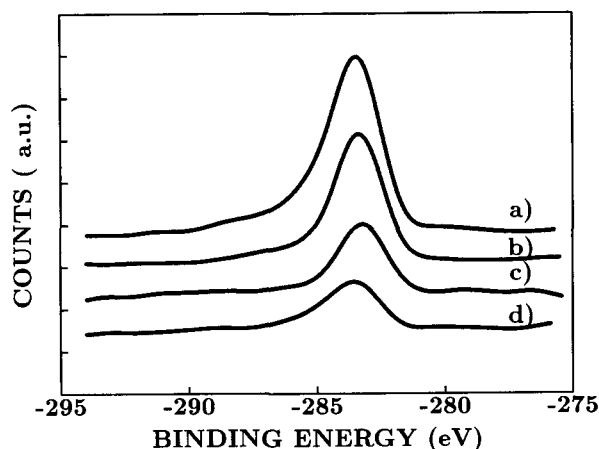Alternatively we have also used the attenuation of the

FIG. 2. XPS spectra in the region of the C 1s peak of a CdZnTe substrate after heat treatment at (a) 30 °C (b) 150 °C, (c) 240 °C, and (d) 300 °C, with an Al $K\alpha$ source.
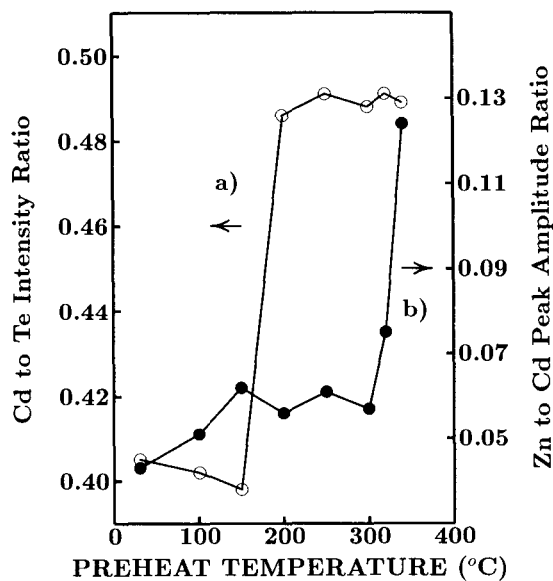
FIG. 3. The intensity ratio of Cd to Te and Zn to Cd for a CdZnTe substrate vs heat treatment temperature, with a Mg $K\alpha$ x-ray source: (a) the ratio of the XPS intensity of the Cd $3d_{3/2}$ core level to that of Te vs heat treatment temperature. (b) The ratio of the Zn $L_3M_{45}M_{45}$ amplitude to that of the Cd $3d_{3/2}$ core level as a function of heat treatment temperature. These amplitudes have been divided by the corresponding background signal.

Cd$3d_{3/2}$ core level peak to determine the carbon thickness according to

$$I_d = I_\infty \exp\left(-\frac{d}{\lambda}\right) \qquad (2)$$

where the escape depth of the Cd$3d_{3/2}$ photoelectrons for the Mg$K\alpha$ x-ray source was 18 Å according to $\lambda \sim E^{0.75}$. Thus we have compared the intensity of the Cd$3d_{3/2}$ core level of a (100)CdTe buffer layer displaying half order reconstructions in the (011), (010), and (001) azimuths with that of a CdZnTe substrate after heat treatment at 300 °C. This resulted in a carbon thickness of about 0.2 Å or about 10% of a monolayer which is within experimental uncertainty the same as that mentioned above.

The above-mentioned thermal treatment greatly influences the surface structure. The ratio of the x-ray photoelectron intensity 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 Fig. 3. Here the measurement error was about 0.01. In contrast the ratio of the relative amplitudes 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 when the temperature was larger than 300 °C, as indicated by curve b in Fig. 3. Here the background changed less than 1%. From curve b in Fig. 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 CdZnTe substrates and cannot be neglected. Based on the results of

earlier CdTe surface studies[18] and Fig. 3, we conclude that the CdZnTe surface is stoichiometric at temperatures between 200 and 300 °C.

Benson *et al.* have measured Zn and Cd surface lifetimes on (100) ZnTe.[19] Even though this system is only slightly related to ours it is interesting that they found the Zn desorption time was about five times as large as that of Cd at 300 °C.

In conclusion, heating CdZnTe substrates at 300 °C 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. The Cd$3d_{3/2}$–Te$3d_{3/2}$ photoelectron intensity ratio increases from about 0.40 to 0.49 when the temperature is raised from 150 to 200 °C. Even more dramatic is the change in the ratio of the Zn$L_3M_{45}M_{45}$ Auger peak intensity to that of the Cd$3d_{3/2}$ photoelectron intensity which increases from about 0.06 to 0.12 when the temperature is raised from 300 to 340 °C. Obviously heat treatment at temperatures higher than about 300 °C could have adverse effects on the MBE growth of lattice matched films.

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