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Study of the Effect of Various Chemical Polishing Treatments on MBE-Grown CdTe/GaAs (211)B Heterostructures

Elif BİLGİLİSOY¹, Elif ÖZÇERİ², Enver TARHAN³

Abstract

A three-inch-diameter high quality CdTe thin film was grown on a GaAs (211)B substrate by molecular beam epitaxy (MBE) in ultra-high vacuum conditions. The CdTe/GaAs (211)B heterostructure was then cut into several sample pieces. A few as-grown sample pieces were subjected to chemical etching solutions which created etch pits on the surface. The scanning electron microscopy images of such samples were used to calculate the etch pit densities on the surface. In addition, several as-grown samples were subjected to chemical polishing treatments under different conditions to quantify the removal of O and Te-O structures from the surface. Atomic force microscopy was used to determine as-grown and polished surface morphology and the polish rate of chemical solutions. A study of the surface stoichiometry and the chemical composition of the as-grown and polished CdTe (211)B surfaces were carried out by using X-ray photoelectron spectroscopy. Bulk structural qualities of the as-grown and polished samples were studied in terms of the vibrational and phonon modes via confocal Raman spectroscopy. From a comparative analyses of the results, the best chemical polishing conditions for the MBE-grown CdTe (211)B heterostructure were determined.

Keywords: Molecular beam epitaxy, CdTe thin film, GaAs substrate, thin film polishing, XPS, Raman spectroscopy, AFM

1. INTRODUCTION

The cadmium telluride (CdTe) – gallium arsenide (GaAs) heterostructure is one of the most important material structures for various applications, such as; imaging and sensing systems [1,2], solar cells [3,4], and digital information storage devices [5]. CdTe is a II-VI ionic semiconductor with a zinc-blende crystal structure. Due to its

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room temperature (RT) band gap energy being 1.47 eV with a direct gap, CdTe can absorb most of the solar radiation [6]. In addition to infrared and visible light detection, CdTe based detectors are widely used for the detection of X-rays and γ radiation, which are especially needed in the fields of medicine, astrophysics, solar energy conversion, and electro-optical modulation applications [7]. Furthermore, CdTe is commonly used as a buffer layer for HgCdTe (MCT) which is one of the most widely used materials for infrared detectors [8,9]. For the growth of MCT, the most widely used substrate is CdZnTe (CZT). By adjusting the Cd/Zn ratio during the growth, the best lattice parameter match can be achieved [7]. However, due to the difficulties to obtain large area and high quality CZT substrates, GaAs wafers are among the best substrate choices. There are many studies on GaAs(211)B substrates which especially show suppression of twin defect formations in MCT [10]. CdTe is commonly used as a buffer layer for MCT on GaAs to minimize the lattice mismatch between MCT and GaAs which is a detrimental effect that causes defect formation such as misfit dislocations, [11–13].

Epitaxial growth of these films by molecular beam epitaxy (MBE) allows the manufacture of high quality materials which are not easily available or very expensive in the bulk form. These thin films are of fundamental importance for microelectronic and optoelectronic technologies. In hetero-epitaxial films, the interfaces greatly affect the subsequent junction performance. For this reason, before the hetero-epitaxial growth of the films on CdTe, it is crucial to study the effect of the preparation treatments on the film surface. To achieve high performance devices, the native oxide layer or oxygen defects on the surface of a material (such as CdTe), which are among the most prevalent defects, must be removed for hetero-epitaxial growth of thin films on them. A coherent native oxide layer grows on CdTe under the influence of UV light in ambient conditions. Oxygen atoms originating from air diffuse through the CdTe lattice mostly replacing Cd atoms [14]. Before growing heteroepitaxial layers on substrates, their surfaces must be prepared.

Among the most common ways of surface preparation are chemical etching and chemical polishing methods with certain solutions which are the main focus of this work [15,16]. While removing the native oxide layer at the top, these treatments also give the opportunity for a detailed analysis of the chemical composition and structure of the layers of the film under the oxide layer.

For the removal of oxide layers and surface defects, several methods involving various etching and polishing solutions are reported in the literature. Chemical polishing is used for a slow and controlled removal of top layers via chemical solutions. The most widely used and standard polishing solution for elimination of Te-oxides from the surface is a Br2 – MeOH (methanol) solution [15,16]. In these studies, it was reported that a shiny and residue-free surface was obtained prior to further treatments. However, in another study, it was stated that Br2 – MeOH solution leaves a very thin amorphous-Te layer on the polished surface [17]. In another study, it was reported that iodine is less corrosive than bromine and reacts with the crystal surface at a lower rate which results a gentle polishing of the surface [18,19]. The most widely used low rate interacting iodine-based solutions are I2 - MeOH [19] and KIO3 - KI - Lactic acid [20] which are also suitable for CdTe-based surfaces [21].

In contrast to polishing, etching is a fast removal of many layers of a sample surface which requires stronger solutions (acids or bases) than those used for polishing. For CdTe surfaces, etching solutions containing HCl and Br2 - Ethylene glycol have already been reported [17,22]. Even though there are many studies in literature about the effects of polishing and etching treatments, to our knowledge, there is no comprehensive investigation comparing the effects of the most widely used polishing and etching solutions on CdTe film surfaces grown on GaAs substrates for further epitaxial treatments. The major goal of this study is, thus, to establish a comparative understanding of several widely used etching and polishing solutions on the chemical composition (hence stoichiometry) of the layers below the surface of an MBE grown CdTe film on a GaAs
substrate, in terms of the concentrations of Cd, Te, and oxygen atoms on or near the film surface after removal of the top layers.

2. EXPERIMENTAL METHODS

A highly crystalline thin layer of CdTe was-grown on a 3-inch epi-ready GaAs (211)B substrate in a Veeco GEN20MZ MBE system. The growth procedure was as follows: After placing the GaAs substrate in the growth chamber, first, the oxide layer on the substrate was removed under In flux while the temperature of the substrate was measured by a band-edge thermometer (BandiT). For that purpose, when temperature of the substrate reached 534 °C, In flux was started at $4.43 \times 10^{-8}$ torr beam equivalent pressure (BEP), which was continued for 300 seconds until the substrate temperature reached 554 °C. The substrate was then kept at this temperature for 330 seconds for the desorption of In compounds (InAs, InO2). Structural properties of the surface during thermal deoxidation was observed by an in-situ reflection high-energy electron diffraction (RHEED) system. Then, the deoxidized substrate was cooled down to 200 °C under As4 flux to assure that the surface of the CdTe film to be grown on the substrate had an As terminated polar face. Next, a nucleation layer of CdTe was-grown for 10 minutes followed by an annealing at 385 °C for 4 minutes. Finally, the substrate temperature was reduced to 300 °C and the growth of the CdTe layer was started. The growth continued until the thickness of the CdTe layer reached 6 µm. During the growth, the substrate was rotated with 2 revolutions per minute (rpm) to ensure a uniform growth profile.

When the growth was completed, the as-grown 3-inch CdTe film on the GaAs substrate was cut into several pieces. A few of them were used as reference; one of which was transferred to the XPS chamber while another one was transferred to the XRD chamber quickly for reference measurements. Both measurements were carried out almost simultaneously only a few minutes after the growth was completed. The other pieces were subjected to various chemical etching and polishing procedures. Each sample, treated or untreated, was then analyzed and characterized. All chemically treated samples were placed in XRD and XPS chambers in a very short duration (a few minutes) after the treatment was ended to minimize contamination from air. Finally, the results were compared and discussed. The methods and characterizations used in this study are given more or less in the following order:

The crystal structure of an as-grown (reference) sample was analyzed using a Philips X'Pert Pro MRD X-Ray Diffraction (XRD) system equipped with a Cu-Kα-alpha X-ray source. X-ray double crystal rocking curve (DCRC) analyses of the peaks from CdTe (422) planes measured at [0-11] and [-111] azimuths were carried out. Full width at half maximum (FWHM) values of the peaks were studied to assess the crystal quality of the as-grown film [23].

The growth of CdTe on GaAs substrate results in dislocations because of lattice and thermal expansion coefficient mismatches of the films. Next analysis was the study of the density of dislocation defects, which is the average number of dislocations per unit area, on or near the film surface to assess the crystal quality of the as-grown CdTe wafer. Dislocation related defects can be revealed on a film surface by a suitable wet chemical etching method. The methods used to calculate the dislocation densities of as-grown CdTe films were explained in detail in our previous studies [23,24]. For that purpose, the process, named as defect decoration, was carried out in three main steps; oxidation, dissolution, and dilution [25]. The etching rate of a film was controlled by varying the parameters of these steps. In the first step, oxidizing agents were used such as bromine, chromic acid, nitric acid, and hydrogen peroxide. Oxidization occurs by taking an electron from a surface Te atom by an oxidizing agent molecule since Te is more reactive than Cd. SEM micrograph images of the etched film surfaces were then investigated visually for etch pits which take place at the surface end of dislocation defects in the film. Then, depending on the etching solution, surface polarity, and the crystal orientation, surface pits with certain geometric shapes were observed by eye from these images.
Two different etching solutions were used to calculate the etch pit densities (EPDs). One of them was an Everson solution (1HF:4HNO3:25C2H4OHCOOH) \[26\] which was applied for 25 seconds at room temperature (RT). The other one was a Nakagawa solution (1HF:2H2O2:2H2O) \[27\] applied for 7 seconds at RT. Then, the etched films were rinsed in DI-water and dried under dry N2 gas flow. The EPDs were calculated by manually counting the number of pits for any given area from the SEM images (obtained by a FEI Quanta 250 FEG system) of the etched samples. The EPD value for a particular sample surface was then calculated as the average of such numbers per unit sample surface area.

The oxide layer was studied with various chemical polishing methods \[15,16\] in order to understand the nature of oxygen contamination on the surface of CdTe films as well as to obtain the concentrations of Cd and Te atoms near the surface. Chemical polishing of the native oxide and the top surface layers of the CdTe films were carried out with several distinct solutions of chemicals such as hydrofluoric acid and hydrochloric acid \[3\]. In the last step, the solutions were diluted by DI water, lactic acid, acetic acid etc. \[10\]. Table 1 lists five different polishing solutions for five samples (named E1, E2, etc.). All sample pieces were cut from the middle section of the wafer to ensure uniformity. A study about the uniformity of similar CdTe/GaAs wafers grown by MBE by the same group of authors is given in the literature \[28\]. Each polishing was followed by a rinsing solution involving a methanol (MeOH) solution and DI water and ended with a dry nitrogen flux. The etching rates of the polishing solutions were calculated by a Solver Pro 7 atomic force microscopy (AFM) instrument (NT-MDT) system. The root mean square (RMS) surface roughness values of as-grown and chemically polished CdTe films were obtained from the topography images recorded in the tapping mode of the AFM system in a class-100 cleanroom environment.

Atomic concentrations of oxide agents on the surface of the chemically treated and untreated samples were studied by X-ray photoelectron spectroscopy (XPS) (SPECS EA200 XPS system). The XPS system is composed of an Al X-ray source and a Phoibos 150 hemispherical analyzer with a 3D-DLD detector. To reduce the noise in the XPS spectra, a large area focus and a 40 eV E-pass energy was used. After the growth, when the CdTe film was cut into several pieces, one sample piece was immediately transferred to the XPS system under the atmospheric conditions. The transfer did not last more than 5 minutes. The same transfer duration was taken for all other sample pieces right after chemical polishing and etching treatments in order to minimize the contamination during the transfer. All XPS...
spectra were calibrated with respect to C-1s peak position at 284 eV. After a linear background subtraction, each spectrum was deconvoluted, using a mixed Gaussian–Lorentzian profile for each individual component, with the help of a CasaXPS software.

After an initial compositional analysis by XPS, each film was then further analyzed structurally by confocal Raman spectroscopy. The structural quality of a film near the surface was assessed by studying the intensity ratio of the 2LO Raman peak to that of the LO peak [23]. This procedure was used both for the as-grown and chemically polished samples. Raman measurements were carried out at various temperatures ranging from RT to 80 K to monitor the changes in the 2LO/LO intensity ratios for comparison. Especially, the Raman data taken at 80 K was used for analyses since it gave the best phonon mode intensities and also provided a better comparison with those in the literature. The temperature of the samples was changed in a controlled manner in a Linkam (THMS600E) cooling chamber with proper optical windows placed under the objective of the microscope of our confocal Raman system. The employed Raman system (an S&I Mono Vista System) consists of an Ar-Ion laser operating at 488 nm and 514 nm wavelengths each with a 120 mW exit power. We employed the 488 nm excitation line since it is in resonance with the energy separation between the top of the Γ7 split-off valence band and the bottom of the Γ6 conduction band in the energy-momentum space of CdTe [30], which intensifies most of the observable (especially the LO and 2LO) Raman peaks of CdTe. The scattered light was then collected by the objective of an Olympus BX51 microscope. After a proper filtering of the Rayleigh line with a narrow band (~100 cm-1) notch filter, the scattered light was directed onto an entrance slit of an ACTON SP2750 Princeton Instruments monochromator with a 750 mm focal length and a set of three holographic gratings (150, 600, and 1800 grooves/mm). The dispersed light from the monochromator was then focused on to the exit slit of the monochromator where it was collected by a high resolution charge-coupled device (CCD) detector. The recorded signal by the CCD was then converted into digital data and sent to the controlling computer to be analyzed as spectrum.

3. RESULTS AND DISCUSSIONS

An example of a high resolution double crystal rocking curve (DCRC) measurement of X-rays scattered from (422) planes of an as-grown CdTe on GaAs (211)B sample is given in Figure 1. The peak centered at 35.61 degree was measured at [0-11] azimuth direction. It has a full width at half maximum (FWHM) value of 75.24 arcseconds. Another DCRC measurement taken at [-111] direction gives a FWHM value of 58.2 arcseconds. Considering that the thickness of the CdTe film is about 6 µm, these values are very close to those of good quality MBE grown CdTe on GaAs samples given in the literature for similar thicknesses [16,17]. Hence, we can say that our CdTe film has a good crystal structure for the (211) surface orientation [17,18].

Next, we focused on the study of etch pit densities (EPD). Figure 2 (a) and (c) are the SEM images of sample A etched with an Everson solution for 15 seconds recorded at 20 kV resolution with 50- and 10-micron scales, respectively. Figure 2 (b) and (d) show 10 kV SEM images of sample B etched with a Nakagawa solution with 50- and 10-
micron scale bars, respectively. For sample A, the dislocation-induced etch pit density (EPD) was calculated as $1.2 \times 10^7 \text{cm}^{-2}$ from these images by the manual counting method as given earlier [26,33]. It is seen that Everson etched sample surfaces exhibit triangular shaped etch pits that are concentrated at certain type of surface defects only. The etch pits formed after the Nakagawa etching are larger than those formed after the Everson etching with some degree of overlaps between some of the adjacent pits. These overlaps and the shape differences indicate that the Nakagawa solution acts on different type of surface defects than those observed with the Everson method. We also observed that the Nakagawa etching technique eroded surface defects caused under Te rich growth conditions. Hence, we can conclude that the Nakagawa etch pits form in the regions of Te precipitates [34] while the Everson etch pits form at dislocation sites. We did not calculate any EPD value for sample B due to overlapping pits.

For the study of the surface stoichiometry and chemical structure of the as-grown and chemically polished samples (see Table 1), we utilized X-ray photoelectron spectroscopy (XPS). A collection of XPS spectra of an as-grown sample and chemically polished samples are displayed in Figure 3. Figure 3 (a), (b), and (c) show the XPS spectra of the as-grown sample piece displaying cadmium (Cd-3d3/2), oxygen (O-1s), and tellurium (Te-3d3/2) peaks, in that order, along with their theoretical fits. A linear background subtraction was used for all experimental data before the fittings. The Cd-3d3/2 peak seen in Figure 3 (a) results from the Te-Cd bonds. We could not see any peak originating from the Cd-O structure. The band observed in Figure 3 (b) is made of two subbands as seen from the theoretical fittings, the one at 533 eV is due to oxygen 1s electrons while the other centered at 531.5 eV indicates a Te-O complex [35]. Figure 3 (c) shows a Te-3d3/2 spectrum that has two components centered at 586 and 582 eV. The 582-eV peak is a Te-Cd peak which originates from the CdTe film and the other one is a Te-O peak which is due to the oxidation of tellurium [36]. Figure 3 (d) shows the Te-3d3/2 spectra of five chemically polished samples (E1,...,E5) as given in Table 1. Each spectrum in (d) shows a strong Te-3d3/2 peak and a weak Te-O peak with a smaller FWHM value.

Figure 2 SEM images of samples A and B etched with Everson and Nakagawa solutions, respectively. Insets (a) and (c) are for sample A with 50- and 10-micron scale bars while (b) and (d) are for sample B with 50- and 10-micron scale bars.
In all XPS results, the Te-O peak indicates a 3.54 ± 0.01 eV higher binding energy than that of the Te-Cd structure. Also it is seen that cadmium bonds only with Te.

One must consider that XPS signal comes mostly from a few top surface layers, hence, it reveals mostly the surface or near surface structure of the samples.

Figure 3 XPS results of (a) Cd-3d3/2, (b) O-1s, and (c) Te-3d3/2 scan of the as-grown CdTe sample. Black dots are experimental data while the continuous red and blue lines are the fit curves. (d) Te-3d3/2 scan of the wet chemically polished CdTe surfaces
The lack of other Cd compounds such as Cd-O structures on the surface indicate that the as-grown film surface ends with Te. Furthermore, the O-1s peak was fitted with two oxygen peaks instead of a single one, which are O-1s and Te-O peaks as seen in Figure 3 (b). We were able to calculate the elemental compositions of Te, Cd, and O at the surface of a film from the Te-Cd, Te-O, Cd-3d3/2, and O-1s XPS peaks. Such calculations were carried out based on the spectra obtained from different regions of the films where the contribution of the relative sensitivity factor (RSF) of each fitting to a spectrum was also taken into account [36].

The results of our elemental concentration (atomic percentages: at. %) analyses obtained from the XPS spectra of the as-grown sample piece and five chemically polished samples are collected in Table 2. Clearly, for the as-grown sample a Cd and Te-O rich surface was seen right after the growth. Its Cd concentration ratio was about 58% which was reduced down to about 40% for all polished samples. While the ratio of Te bound to Cd was about 27% in the as-grown sample it increased to 53-60% range for the polished samples. Additionally, the concentration of the oxidized Te for the as-grown sample was 18% which dropped down to 3 percent or less for the polished samples. These results indicate that the as-grown film surface was indeed Te terminated and a native oxide layer was formed on top of it right after its exposure to ambient air. We also see that the samples E2 and E3 show no oxygen concentration at all. Thus, the chemical polishing methods employed for these samples effectively removed all of the oxygen atoms located on or near the surface. Another point is that we see a smaller Cd concentration for the sample E1. This suggests that the solution used to polish that sample (see Table 1) aggressively eroded Cd-Te and Te-O structures.

We also notice that, the concentration of Te-Cd bonds increased from about 27 percent for the as-grown sample to nearly 60 percent for the polished samples. This leads us to conclude that the Te-rich layers are limited only to the upper layers of the as-grown film, hence, the stoichiometry of the deeper layers is more regular.

| Samples  | Cd (at. %) | Te-Cd (at. %) | Te-O (at. %) |
|----------|------------|---------------|--------------|
| As-grown | 58.34      | 26.66         | 18           |
| E1       | 38.49      | 58.38         | 3.13         |
| E2       | 46.14      | 53.86         | 0            |
| E3       | 40.32      | 59.68         | 0            |
| E4       | 40.85      | 56.07         | 3.08         |
| E5       | 40.23      | 57.79         | 1.97         |

The fact that the ratio of oxidized Te is very close to that of Cd bound Te for the as-grown sample indicates that Te atoms form Te-Te dimers or multiple structures instead of Cd-Te bonds at the defect centers in the CdTe crystal. These Te-Te structures are then easily oxidized when exposed to atmospheric conditions yielding Te-O peaks in the XPS spectra. Similarly, high oxygen content observed in the films reveal that the film surfaces are very rich in Te. To clarify this point and to further analyze the quality of the as-grown film, we also carried out Raman spectroscopy measurements on all polished samples mentioned so far.

Raman spectra of the samples were recorded at 80 K after completing their XPS analyses to obtain information about the crystal quality of the chemically polished films and to determine how the chemical polishing methods affected the hetero-epitaxially grown CdTe film quality. Figure 4 shows several Raman peaks that are related to the fundamental TO (Transverse Optic), LO (Longitudinal Optic) and 2LO phonon modes of CdTe crystal structure [37]. The peaks labelled as E and A1 are due to vibrations of Te-Te structures. Generally, in the Raman spectra of all samples the intensities of A1 vibrational modes of Te-Te structures were greater than those of Cd-samples, the intensities of A1 Te phonon modes (TO, LO and 2LO). Figure 4 (a) and (b) show theoretical fittings to the observed spectra.
The fittings were carried out using a Person VII type fitting function which is basically a generalized Lorentzian function to an arbitrary integer power [38]. It is seen that the TO and LO phonon modes of all polished CdTe films are at about 141 cm⁻¹ and 168 cm⁻¹, respectively, which are almost the same as those of a bulk CdTe crystal [39]. It is well known that when there is stress in the crystal, the frequencies of these modes blueshift to higher values. All our samples (which are obtained from the same as-grown film) used in this study, show blueshifts of a few (about 2) wavenumbers only, indicating a relatively small stress in the crystal structure. Thus, it is safe to conclude that all our samples, before and after polishing, show high crystal quality.

LO phonon modes are electric dipole forbidden in the Raman backscattering geometry. This is because an LO phonon carry a large momentum and photon scattering cannot account for such a momentum exchange since visible photon momenta are much smaller than those of LO phonons. Various mechanisms have been proposed to explain the nature of the experimentally observed LO mode peaks in the Raman spectra of III-V and II-VI semiconductors. These are mainly; deformation potential scattering [40], impurity mediated scattering [39,41], and exciton (electron-hole pair) mediated scattering which is due to long range Fröhlich interactions [40,42]. Contrarily, multiphonon modes may be dipole allowed. Especially, when two LO phonons of opposite momentum (from the opposite regions of the first Brillouin zone of phonon energy-momentum space) are created simultaneously, their sum may carry almost zero momentum, hence, requiring no net momentum transfer [32]. This point will be discussed further below.
The room temperature Raman spectra of most CdTe samples are dominated by Te precipitates on the surface [43]. However, in the case of resonant Raman scattering (RRS), at low temperatures, Raman intensities of the intrinsic phonon modes become much more pronounced [29,40,42]. We clearly see that the observed RRS at low temperatures (80 K) were dominated by phonon modes of CdTe as seen in Figure 4. Thus, to minimize the surface effects on the observation of phonon modes in Raman spectra, we carried out measurements at 80 K. Indeed, our RT Raman measurements do not yield strong phonon modes and we do not show them here.

Table 3 summarizes the results of our Raman measurements. The peak intensities of A and E modes of Te precipitates on the polished samples are normalized with respect to that of the as-grown sample. We also show the 2LO/LO intensity ratios for all polished samples and the as-grown sample. Although the A1 mode intensity increases for all samples except for the sample E1, there is a clear reduction in the intensity of the E mode of Te in all polished samples. This suggests that polishing removed some of the Te precipitates from the surface albeit not totally. Only in the sample E1 the removal is quite substantial. We will discuss this sample again below.

Table 3
Raman intensities of A1 and E modes of Te-Te vibrations of polished samples normalized with respect to that of the as-grown sample along with the 2LO/LO intensity ratios of all polished samples and the as-grown sample. All measurements were carried out at 80 K.

| Samples | Normalized A1 int. | Normalized E int. | 2LO/LO |
|---------|-------------------|-------------------|--------|
| As-grown | -                 | -                 | 2.61   |
| E1      | 0.8               | 0.4               | 2.38   |
| E2      | 2.1               | 0.5               | 1.86   |
| E3      | 1.3               | 0.1               | 2.26   |
| E4      | 1.6               | 0.4               | 2.16   |
| E5      | 1.3               | 0.1               | 1.88   |

In the case of resonant Raman scattering, since the simultaneous emission of two LO phonons easily satisfy the momentum conservation rule for electric dipole scattering (near zero phonon momentum), in principle, for a good quality sample, the observed 2LO phonon intensity should always be stronger than that of the LO phonon intensity since the latter is either due to impurities or the long range Fröhlich interactions, provided the impurity concentrations are sufficiently low [29,40,42]. We can assume that the observed intensity variations in the Raman spectra of the polished and as-grown samples, which are given by the intensity ratio of 2LO to that of LO phonons (seen as 2LO/LO in Table 3) should be due to the effect of chemical treatment on the polished samples. As we see from the table that the 2LO/LO ratio is highest for the as-grown sample but reduced somewhat in the polished samples. Since, chemical polishing will not change the excitonic effects on LO and 2LO modes because Fröhlich interactions also play a role in the 2LO phonon mechanism [14], there are only two candidates for the increased LO intensities for the polished samples: First one is increases in the impurity concentrations and second one is changes in the deformation potential due to polishing. In principle, we can say that both processes may play a role. Since polishing will remove many surface layers, it might change the crystal potential in the bulk which will increase the role of the deformation potential. However, the observed blueshifts in the LO and 2LO phonon modes are almost the same for both as grown and the polished samples. Which means polishing does not change the crystal potential considerably, and hence, we can rule out its effect on the observed 2LO/LO intensity variations. On the other hand, polishing might increase the impurity concentration in the bulk of the film (although the surface may improve) by removing the protective oxide layer on the surface which may act like a barrier for the penetration of impurities either from the polishing solution or from air. For that reason, we think that the increased impurity concentrations in the polished samples are the major cause of the increased LO phonon intensities. Hence, even though the polishing increases the surface quality of the CdTe samples by removing Te precipitates and the oxide layer, it may decrease the bulk quality somewhat by increasing the impurity.
concentrations. However, in all our polished samples, the possible increase in the impurity concentration cannot be larger than two folds since all 2LO/LO ratios remain in that range. Hence, the reduction in the crystalline quality due to polishing can be ignored safely for small impurity concentrations to improve the surface quality for a suitable set of polishing parameters. Thus, one must find the best chemical polishing conditions to optimize the method. Based on these discussions about our Raman results, the polished samples with the better structural quality should be the samples E1, E3, and E4, in that order.

In order to reach a sound conclusion, we must also discuss the atomic force microscopy (AFM) results. The AFM images were used to obtain information about the surface morphology of the samples and polish rates of the polishing solutions (E1..., E5). Figure 5 (a) shows an AFM image of the as-grown sample while (b) shows that of the polished sample E5. We have calculated the average depths of the pits (local minima) on the surface for as-grown and polished samples from the AFM image data to obtain the polishing rates.

Table 4 gives the polishing rates and durations of all polished samples. Also listed in the table are the RMS roughness values and average topographic local minima (pit) depths of all samples (polished and as-grown) as found from the AFM measurements. We see that the sample E5 has the smallest average pit depth and RMS roughness value. One might say that the polishing parameters (see Table 1) for this sample were optimum for the best quality surface. However, the best samples in terms of internal structure (smaller impurity concentration or smaller structural deformation) are the samples E3 and E4 as seen from Table 3 with the highest 2LO/LO intensity ratios. When the cleanest and the smoothest surface is needed, the best polishing treatment is probably the one used for the sample E5 since it has the best surface quality with a tolerable reduction in the bulk quality for which the 2LO/LO ratio is still high (1.88 versus 2.26 for E3). On the other hand, if one wants to grow a HgCdTe layer for infrared detector applications, probably a Te rich surface is needed. For that purpose, the sample E2 maybe the best choice since it has a good stoichiometry as seen from the XPS results with no native oxide layer, as seen in Table 2, and it also has a very small RMS surface roughness value (Table 4) along with a highest concentration of Raman A1 peak of Te-Te structures, as seen in Figure 4 (c) and also from Table 3, which indicates existence of Te precipitates on the surface needed to start HgCdTe growth at the top [22]. In conclusion, when polishing is necessary to remove the native oxide layer and other unwanted structures on the surface such as Te precipitates, the best polishing procedure to carry out may be the polishing procedure used for the sample E5, that is, polishing with %0.5 Br2 - ethylene glycol for 25 seconds followed by rinsing in ethylene glycol and DI water. But, when a CdTe/GaAs heterostructure such as the one studied in this work is to be used as a substrate for the growth of

![Figure 5 Atomic force microscopy images of (a) as-grown and (b) polished (E5) samples](image-url)
a HgCdTe detector layer at the top, the polishing procedure for the sample E2, that is, 1HCl - 9DI solution for 3 seconds followed by rinsing in DI water, is probably the best choice since it still has very good surface and bulk qualities with some amount of Te precipitates needed for the growth of a HgCdTe layer at the top.

Table 4
Polishing parameters and AFM characterization results

| Samples | Polishing Time (sec) | Polishing Rate (nm/sec) | RMS Roughness (nm) | Average Local Minima Depth (nm) |
|---------|----------------------|-------------------------|--------------------|---------------------------------|
| As-grown | -                    | -                       | 5.6                | 50                              |
| E1      | 25                   | -                       | -                  | -                               |
| E2      | 3                    | 10                      | 3.8                | 18                              |
| E3      | 30                   | 4                       | 9.4                | -                               |
| E4      | 20                   | 2                       | 3.5                | 19                              |
| E5      | 25                   | 2                       | 2.9                | 16                              |

4. CONCLUSIONS

In this study, we grew a 6 μm thick highly crystalline CdTe film on a GaAs (211)B substrate. XRD and AFM measurements carried on the as-grown film indicated a good crystal quality. Then, surface contamination with oxygen was removed by five different chemical polishing solutions. Before wet chemical polishing treatments, the CdTe film included Te-O structures at the surface indicating a Te rich surface. After the wet chemical polishing treatments, almost all solutions removed the native oxide layer perfectly. When we compared the results of all XPS, Raman, and AFM analyses, the most effective polishing solution for the best surface quality was the one used for the sample E5 that is 0.5 Br2 - Ethylene glycol. If the as-grown CdTe film is to be used as a buffer layer for a HgCdTe thin film detector at the top, probably the solution used for the sample E2, that is, 1HCl - 9DI, applied for 3 seconds, is the best choice since it shows a small amount of Te precipitates needed to start HgCdTe growth at the top. Both samples E2 and E5 show good surface and bulk qualities as seen their AFM, XPS, and Raman results.

In conclusion, a detailed comparative study of the effects of several etching and polishing solutions on a high quality MBE grown CdTe/GaAs(211)B film is carried out. The effect of these solutions on the polished CdTe surfaces are discussed. Since each polishing solution removed many layers from the top surface, chemical compositions, hence the stoichiometry of the as-grown film, and natural structural defects beneath the top surface of the as-grown CdTe film were exposed and studied in detail. Our results indicate that best polishing methods are those used for the samples E2 and E5 as given in Table 1.

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The Declaration of Conflict of Interest/Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

E.B: Experimental section, especially chemical polishing and removal procedures, data analysis, discussion of results, and conclusions

E.Ö: General literature review and writing the introduction, XRD, SEM and XPS measurements, general data analysis, discussion of results, and conclusions

E.T: Writing the entire article, general data analysis, discussion of all experimental results, and conclusions

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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