Journal of the Korean Vacuum Society
Vol. 5, No. 1, March 1996, pp. 6~13

Native Oxide Formations on (AL,Ga)As and (Cd, Mn)Te surfaces

Seong Soo Choi
Department of Physics, Sun-Moon University, Ahsan, Chung Nam, Korea 336-840
(Received December 5, 1995)

(A1, Ga)As 와 (Cd, Mn)Te의 복합화합물 반도체표면에서의 자연 산화물의 형성

최 성 수
선문대 물리학과
(1995년 12월 5일 접수)

ABSTRACT – The kinetics of native oxide formation on the (Al, Ga)As and (Cd, Mn)Te have been studied by X-ray photoelectron spectroscopy(XPS) and Auger electron spectroscopy(AES). The regrowth of native oxide after 3keV Ar ion sputter etch and deionized water etch has been studied. The previous report exhibited that the native oxide on CdTe and GaAs can be removed completely by deionzied(DI) water only[1]. On the other hand, the airgrown native oxide on (Al,Ga)As become nonhomogeneous and the regrown native oxide on (Cd,Mn)Te can be partially removed.

요 약 – (A1, Ga)As 와 (Cd, Mn)Te의 표면에 있어 자연 산화물의 형성 과정은 X-ray에 의한 여기된 광전자 분광법과 Auger전자 분광법에 의하여 연구되어져 왔다. 3 keV의 알곤 이온과 이온이 없는 물 세척에 의한 자연 산화물의 제거후의 자연산화물의 재성장이 조사되었다. 예전의 보고서에 의하면 카드늄 텔류라이드(CdTe)와 갈리움 비소 (GaAs)의 자연 산화물은 무이온 물세척으로 완전히 제거되어 질 수 있음을 보혀주고 있다[1]. 반면에 이보고서는 (Al, Ga)As의 자연 산화물은 비동질성을 이루고 (Cd, Mn)Te의 표면에 재 성장된 자연산화물은 부분적으로 제거되어짐을 제시하고 있다.

I. Introduction

There have been many studies related to native oxide formation on GaAs, CdTe and their related compound materials such as (Al, Ga)As and (Cd, Mn)Te[1-17]. The surfaces of the compound semiconductors have been exposed to different oxidizing environments: oxygen, anodizing electric chemical solutions, etc. The chemical composition of the grown native oxide can vary considerably depending upon the oxidizing conditions. The important factor in determining the chemical composition of the native oxide is the extent to which the oxidation process departs from thermal equilibrium conditions. The chemical bindings of the native oxide on the compound semiconductors have been studied in a variety of different ways: X-ray photoelectron spectroscopy(XPS), ellipsometry, Auger electron spectroscopy(AES), etc. In this paper, we will address (a) the native oxide removal by DI water only, free of the chemical contaminants, (b) the characterization of the nature of grown native oxide.

II. Experimental Procedure

The studies related to the GaAs and (Al, Ga) As surfaces were performed on the (100) sur-

faces of either bulk-grown GaAs wafers or MBE grown thin films on the GaAs substrate, while the studies on the $Cd_{0.8}Mn_{0.2}Te$ surface were performed on the (100) surface of the bulkgrown $Cd_{0.8}Mn_{0.2}Te$ sample. All the samples were degreased by methanol, trichloroethylene(TCE), acetone prior to DI water rinsing. All of the spectra were obtained using a high resoultion surface analysis instruments such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy(XPS). The X-ray sources employed were Mg/Al dual anodes with a characteristic X-ray energy of 1253. 6eV and 1486.6eV, correspondingly. XPS spectra were obtained in a multiplex, repetitive scan mode, while the spectra for Auger electron spectroscopy (AES) were obtained in a survey spectrum mode. AES is better suitable for the light elements such as Al, while XPS is suitable for the heavier elements such as Cd, Mn, Te, Ga and As due to the instrumental sensitivities for each elements.

In general, the following procedures were used: (i) all of the GaAs, (Al, Ga)As, (Cd, Mn)Te samples were initially studied using XPS and X-ray excited AES in order to determine the "as-received " surface oxide chemistry, e.g., the presence of native oxides, surface carbon, etc., (ii) the surfaces were degreased to remove hydrocarbons, and then either subjected to sputtering etching in the UHV surface analysis chamber, or DI water etching prior to insertion of the samples to the introduction chamber of the UHV analysis chamber to remove any native oxides; (iii) the etched, oxide-free surfaces were then exposed to "moist laboratory air" with relative humidity in the range of 30% to 50% and new oxide layers were grown; (iv) then the new native oxide layers were examined by AES, XPS and X-ray excited AES; and finally, (v) this " second generation" of airgrown native oxide layers was rinsed by deionized water, and the resulting surfaces were once more characterized by AES, XPS and X-ray excited AES.

III. Results

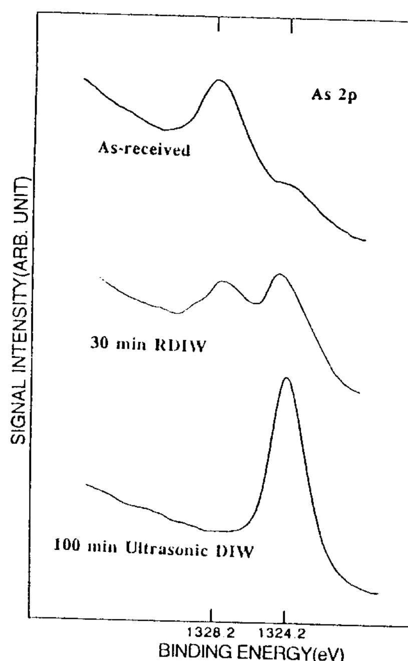

Fig. 1. As 2p XPS spectra: (a) as-received, (b) after 30 min. rinse in running DI water, (c) after 100 min. rinse in DI water in an ultrasonic cleaner.

The studies will be presented in the following way; spectra related to native oxides (i) on the GaAs surface, (ii) on the $Al_{0.7}Ga_{0.3}As$ surface and (iii) on the $Cd_{0.8}Mn_{0.2}Te$.

(i) Native Oxide studies on GaAs:

Fig 1 and 2 displays the As 2P peak XPS spectra and the Ga LMM X-ray induced AES spectra, respectively. Consider first As 2P XPS data in Fig. 1 The as-received surface displaces a two peak structure. Previous studies[2, 3, 4] have established that the lower energy doublet features at about 1324eV is associated with As-Ga bonding (as in GaAs), and the higher energy feature at about 1328eV is associated with As-O bonding (as in As_2O_3). The ratio of intensities of these two features gives a measure of the relative As-O bonding which clearly dominates. Note that a 30 minute rinse in running deionized water(RDIW) clearly reduces the fraction of As-O bonding, and that a 100 minute rinse in DI water in an ultrasonic cleaner eliminates entirely the higher en-

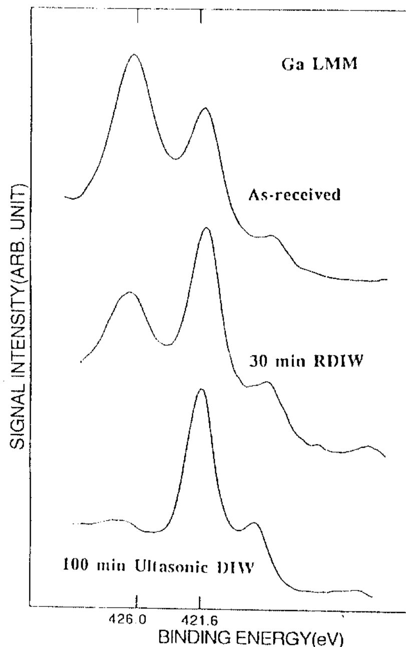

Fig. 2. Ga LMM X-ray excited AES spectra: (a) as-received, (b) after 30 min. rinse in running DI water, and (c) after 100min. rinse in Di water in an ultrasonic cleaner.

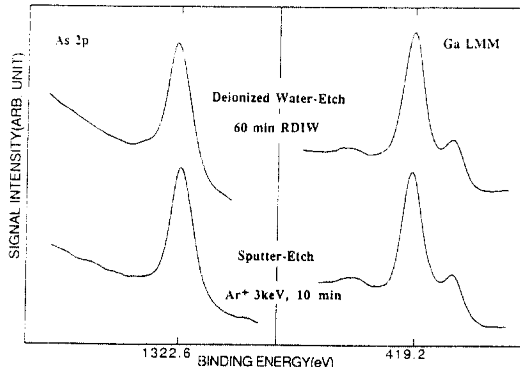

Fig. 3. As 2p XPS spectra Ga LMM X-ray excited AES spectra after native oxide removal by: (a) a 60 min. rinse running DI water and (b) a 10 min. sputter etch using 3keV Ar ions.

ergy, As-O feature. Fig. 2 presents similar data for the Ga spectral feature, i.e., the LMM X-ray induced AES peak. We have used this peak, rather than a Ga 3d XPS peak, because it provides a better measure of the ratio of Ga-As and Ga-O bonding fraction[3, 4]. The higher energy feature in the Ga LMM X-ray induced AES spectrum at about 425eV is associated to Ga-O bonds, and the lower energy feature at 420eV, with Ga-As bonds. Note that the ratio of the relative intensities is reduced by more than a factor of two for rinsing in RDIW for 30 minutes, and by more than a factor of ten for rinsing for 100 minutes in DI water in an ultrasonic cleaner. Note that the spectrum for 100 minute rinse shows an additional small feature at the same position of the Ga-O feature in order to determine whether this is due to residual Ga-O bonding, or is characteristic of the Ga-As bonding, we compare in Figure 3 the As 2P peak and the Ga LMM peak features for surface in which the native oxide layers were removed respectively: (1) by in-situ sputter etching with 3 keV Ar ions in the analysis chamber, and (2) by dissolution in DI water for 60 minutes in an ultrasonic cleaner, and RDIW for 60 minutes. The As 2P peak and the Ga LMM spectra are indistinguishable for two different methods of native oxide removal and this leads us to conclude that the residual feature near 426eV in the Ga LMM spectra is inherent to Ga-As bonding, as in GaAs.

The As 2P XPS peak and the Ga LMM peak in Figure 4 for the oxides grown in water were also examined. Both the As 2P and the Ga LMM bands show the doublet structures indicative of the As-O and Ga-O groups. The relative peak ratio, i.e., As-O/As-Ga and Ga-O/Ga-As in this figure are comparable to the relative peak heights of the same feature as shown in Fig. 1 and Fig. 2 for air-grown native oxides. These oxides were formed after the surface had been cleaned by rinsing in DI water for about 30 minutes. The resulting spectra indicate that the As-O satellite line is totally absent in the As 2P XPS spectrum, but the Ga-O satellite feature is still present in the Ga LMM X-ray AES spectrum after a 100 minute rinse in RDIW. Our studies also indicate that from the relative intensities of As-O XPS and the Ga-O X-ray induced AES features, the oxide layer grown in water in the absence of laser irradiation is comparable

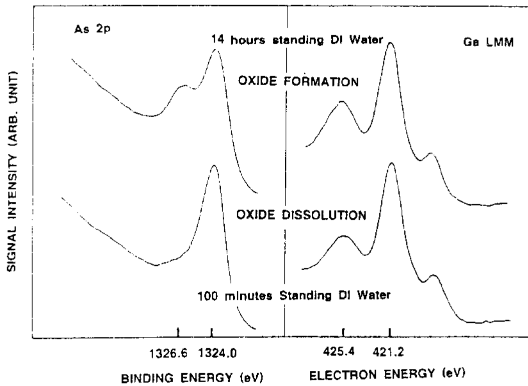

Fig. 4. As 2p XPS spectra and Ga LMM X-ray excited AES spectra: for (a) oxide formation and (b) oxide removal in standing DI water.

in thickness to the native oxide formed in air, and is of the order of 20-50Å thick, but our experimental results indicate that the oxide grown in DI water in the presence of above bandgap laser irradiation is significantly thicker, more than several hundred angstroms thick by considering the electron escape depths. This thickness estimate is in agreement with other estimates of oxides grown in water and under the influence of laser irradiation [5]. After ($Na_2S+9\ H_2O$) treatments our studies by XPS study revealed As-S bonding at 1325.7 eV and no evidence for Ga-S bonding; either in the Ga 2P XPS feature, or Ga LMM X-ray induced AES feature. This result is also in agreement with other reported studies[7].

(ii) Native oxide on $Al_{0.7}Ga_{0.3}As$:

Figure 5 presents AES survey peak for the sample Al 0.7 Ga 0.3 As. Fig. 5(a) presents AES spectra for $Al_{0.7}Ga_{0.3}As$ sample after native oxide removal by Ar 3keV ion sputtering. For light element such as Al, AES has better sensitivity than XPS. Therefore, we have exploited AES rather than XPS for Al surface studies. The Al KLL, LMM transition peak for Al-O bonding (as in Al_2O_3) should have electron kinetic energy at about 1378eV and 51eV, respectively. On the other hand, Al KLL and LMM peak for (Al-Al) bonding should have 1396eV and 68eV, respectively[8].

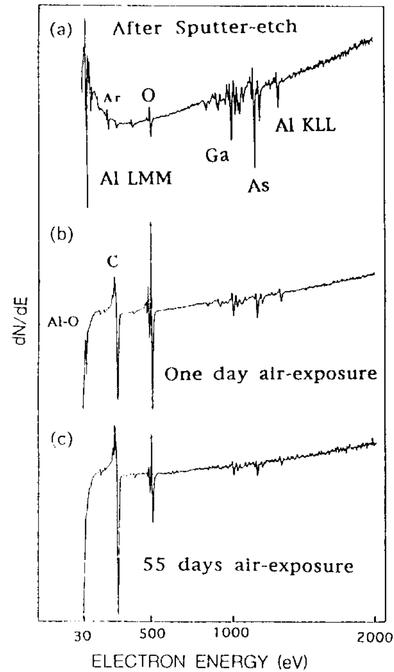

Fig. 5. AES survey spectra for the AlGaAs surface: (a) after 3 keV Ar ion sputte etch, (b) upon one day air-exposure, and (c) upon 55 days air-exposure.

The Ga KLL and the As LMM transition peaks should have 1070eV and 1228eV, respectively. Fig. 5(a) presents a general survey spectrum immediately after the sputter etching in UHV analysis chamber. This survey exhibits the very strong Al LMM peak centered at 65eV, Ar peak at 171eV, oxygen peak at 502eV, Ga LMM feature at 1049eV, and As LMM feature centered at 1206eV, Al KLL feature at 1380eV. Upon air exposure for one day in laboratory environment, the significantly reduced Al LMM peak position with a chemical shift from 65eV to 57 eV was presented in Fig. 5(a) and (b). The oxygen peak position at 502eV and Ar peak position at 212eV were also displayed in Fig. 5(a) just after the sputter-etch in high vacuum analysis chamber. The oxygen peak at 508eV and the carbon peak with significantly increased intensity at 271eV were also observed in Fig. 5(b) upon only one day air-exposure. For the period of upto 55 days air-ex-

posure in Fig. 5(c), the Al LMM peak diappeared completely, while the Al KLL peak are still present.

The electron escape depth for about 60eV and 1380eV is reported to be approximately 2 monolayers and 10 monolayers thick, respectively[9, 10]. When the primary electron energy is 3keV, the relative sensitivities for Al KLL and Al LMM are approximately 0.055 and 0.24, respectively. Hence, one has to be careful for studying Al-O bonding in the native oxide formation. The electrons emitted from Al LMM transition has better sensitivity than that of Al KLL, though it has less escape depth. Fig. 5(c) presented no Al LMM with Al KLL feature still present, which is indicative of nonuniform Al distribution in the grown native oxide on $Al_{0.7}Ga_{0.3}As$. The relative sensitivity for Ga LMM and As LMM is approximately 0.14 and 0.08, respectively[8]. The significant change of the ratio of signal intensities for Al LMM, Ga LMM and As LMM features as displayed in Fig. 5 will be indicative of nonuniform distribution of the each elements in the grown oxide layer. We can deduce that, after initial (Al-O) bonding as in the protective Al_2O_3 is formed, only gallium-oxide and arsenic oxide may be formed on top of the Al-O bonding layer.

(iii) Native oxide on $Cd_{0.8}Mn_{0.2}Te$

The native oxide studies on CdTe and its related compounds were reported previously[1, 11-21]. The inertness of the sputter- etched surface on CdTe were reported before[1, 14]. It normally takes about 3 days for oxide-free surface by chemical etching or DI water-etching to observe Te-O bonding on CdTe (100) surface. It takes one month to observe a Te-O bonding satellite peak for sputter-etched CdTe surface by Ar ion. Figure 6 traces the spectral changes in Te $3d_{5/2}$ and $3d_{3/2}$ features from the $Cd_{0.8}Mn_{0.2}Te$ sample. Fig. 6 presents an "oxide-free" surface on $Cd_{0.8}Mn_{0.2}Te$ after sputter etching by 3keV Ar ion in Fig. 6(a), regrowth of a native oxide upon "10 minute" laboratory air-

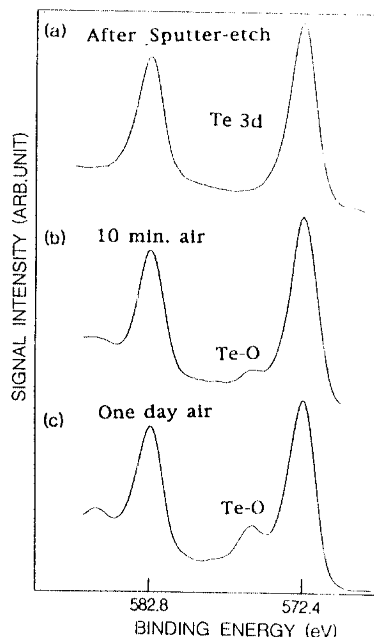

Fig. 6. Te 3d XPS spectra for (a) just sputter etched surface, (b) the surface upon 10min air-exposure, and (c) the surface exposed to air in a laboratory envionment for one day.

exposure in Fig. 6(b), and upon upto "One-day air exposure." in Fig. 6(c). No Te-O bonding are presented and only Te-Cd bondings, Te 3d peaks at 572.4eV and 582.8eV, are displayed in Fig. 6(a). Fig. 6(b) presents the relatively fast formation of Te-O bonding at 576 eV within 10 minutes of air-exposure. Furthermore, for only one day air exposure a significant increase of Te-O satellite peak indicates formation of native oxide.

The development of the oxidized surface on $Cd_{0.8}Mn_{0.2}Te$ for Mn $2P_{3/2}$ and $2P_{1/2}$ during the period of from 10 minutes air exposure upto one day exposure was presented in Figure 7. Mn 2P feature at ~641eV in Fig. 7 (a) indicates " almost" oxide-free surface immediately after Ar sputter-etch in an UHV system. The maganese oxide compounds such as MnO, MnO_2, Mn_2O_3 can have $2P_{3/2}$ binding energies, ~640eV, ~642eV and ~641eV, respectively[22]. The pure Mn have $2P_{3/2}$ at 638.8eV and $2P_{1/2}$ peaks at ~650eV. Fig. 7(b) presented the sig-

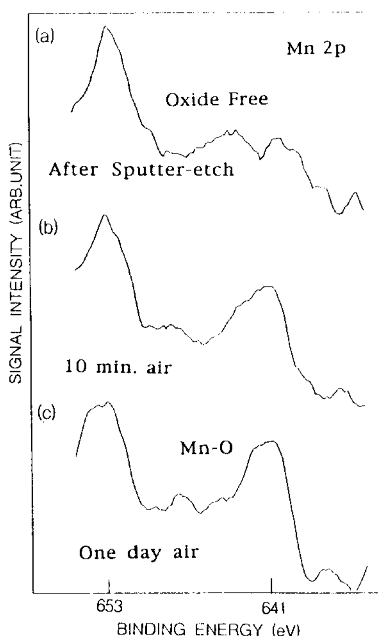

Fig. 7. Mn 2p XPS spectra for (a) oxide free surface by sputter etch, (b) the surface upon 10 min. air-exposure, and (c) the surface exposed to air in a laboratory environment for one day.

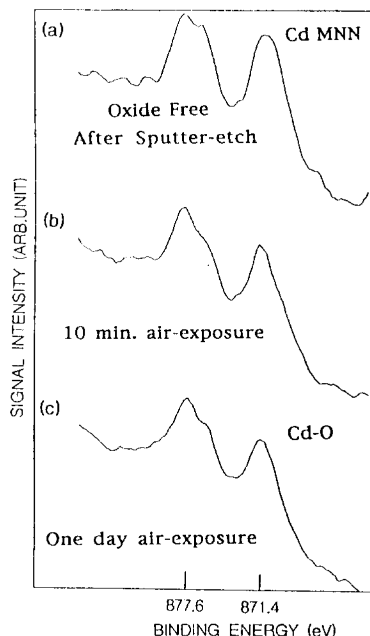

Fig. 8. Cd MNN x-ray excited AES spectra for (a) oxide free surface by sputter etch, (b) the surface upon 10 min. air exposure, and (c) the surface exposed to air in a laboratory environment for one day.

nificant increase of the signal intensity for Mn $2P_{3/2}$ at 641eV, while the Mn 2P peak at 653eV did not change for only 10 min air exposure. After one day laboratory air exposure, higher and broader $2P_{3/2}$ peak at 641eV and extra satellite peak at ~647eV were presented in Fig.7(c).

Figure 8 displays similar data for evolution of the Cd MNN AES features excited by 1253.6eV Mg X-ray. There are some difficulties in analyzing the Cd MNN AES features from the CdTe sample as reported already[1]. The reason is that the Cd MNN AES features from either CdTe or (Cd, Mn) Te do not display distinct doublet splitting for Cd-Te and Cd-O bonding as do the Te 3d features in addition to the spectral overlap between the Cd $M_4N_{45}N_{45}$ feature and the Te $3P_{1/2}$ XPS line[20]. Though, the Cd MNN X-ray AES feaures of the CdMnTe sample may shift in energy and change in shape as does in CdTe. The position of the low energy feature Cd $M_4N_{45}N_{45}$ changes its chape and the region between the two CdMNN features fills in. In addition, there is a significant change in the higher energy feature $M_5N_{45}N_{45}$: (i) noticiable reduction of the lower energy shoulder seen from Fig. 8(a) to Fig. 8(b), (ii) slight increase of the low energy shoulder due to filling of the energy valley region between the two MNN features in Fig. 8(C).

Figure 9 presents Te 3d XPS spectra for time-dependent etching by DI water rinsing of a regrown natrive oxide layer on the $Cd_{0.8}Mn_{0.2}Te$ sample. Fig. 9(a) exhibits a Te-O bondings from regrown native oxide layer upon two day air-exposure. layer by DI water rins The reduced signal intensity of the Te-O bonding peak indicates partial removal of the regrown oxide layer by DI water rinsing for two hours in Fig. 9(b). Fig. 9(c) presents the increased signal intensity for Te-O bonding for 10 hour DI water rinsing. These features present Te-O satellite peaks around 576eV and 586eV in addition to secondary small shoulder near ~576.5eV,

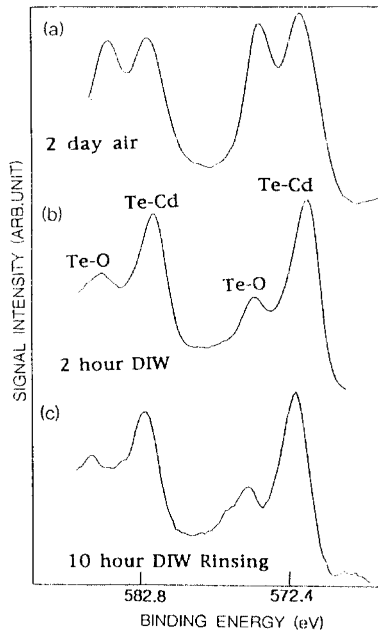

Fig. 9. Te 3d XPS spectra for (a)(the surface for 2 day air exposure after sputter-etch, (b) after 2 hour rinsing in Di water, and (c) after 10 hour rinsing in DI watere.

which means either formation of $Te(OH)_6$ or TeO_3 bonding. These results are quite contrary to the previous results[1], which presented complete native oxide removal by DI water rinsing only.

IV. Conclusion

The results can be summarized as follows; (i) that the air grown native oxide formed on initially oxide-free GaAs(100) surfaces diplays both Ga-O and As-O bonds; (ii) Ga-O bonding is easily detected in the $M_4N_{45}N_{45}$ X-ray excited AES feature, (iii) As-O bonding is readily detected by the formation of double features in the As 2p XPS core level feature, (iv) that GaAs native airgrown oxide are water soluble. (v) the airgrown native oxide on the (Al, Ga)As substrate is nonuniform from the fact that the Al LMM peak decrease very sharply with increasing time exposed to air.

In addition, (vi) the immdediate Te-O bonding formation on $Cd_{0.8}Mn_{0.2}Te$ upon air exposure in laboratory room environment has also been presented. This is quite contrary to the previous results related to oxide formation on the CdTe, which revealed that the surface become very inert after sputtering etching, or very slow oxide formation (2 or 3 days air exposure to exhibit Te-O satellite peaks). Furthermore, for an extended 10 hour DI water rinsing, the increased Te-O peaks, rather than a complete removal of Te-O 3d doublet satellite peaks, presented the formation of nonuniform air grown oxide layers due to the added Mn element.

References

1. S.S. Choi and G. Lucovsky, *J. Vac. Sci. and Technol.* **B6**. 1198(1988).
2. C.D. Thurmond, G.P. Schwartz, G.W. Kammlott and B. Schwartz, *J. Electrochem. Soc.* **127**, 1366(1980)
3. A.C. Warren, S.D. Offsey, J.M. Woodall, P.D. Kirchner, T.I. Chappell, and G.D. Pettit, *J. Vac. Sci. Technol.* **B4**, 1115(1986).
4. G.P. Schwartz, G.J. Gualieri, J.E. Griffiths, C.D. Thurmond and B. Schwartz, *J. Electrochem. Soc.* **127**, 2488(1980).
5. C.W. Wilmsen, P.D. Kirchner, J.A. Baker, J.A. Kash, and J.M. Woodall, *J. Vac. Sci. Technol.* **B6**, 1180(1988).
6. H. Hasegawa, H. Ishii, T. Sawada, T. Saitoh, S. Konishi, Y. Liu, and H. Ohno, *J. Vac. Sci. Technol.* **B4**, 1184(1988).
7. C.J. Sandroff, M.S. Hedge, and C.C. Chang, *J. Vac. Sci. Technol.* **B7**, 841(1989).
8. L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach, and R.E. Weber, Handbook of Auger electron spectroscopy, (Perkin-Elmer Corporation, Eden Prairie, Minesota, 1978).
9. Practical Surface Analysis by Auger and X-ray Photoelectron scopy, edited by D. Briggs and M.P. Seah(Wiely, Chichester, 1983).
10. *Methods of Surface Analysis*, edited by A.W. Czanderna(Elsevier, Amsterdam, 1975).
11. J.P. Haring, J.G. Werthen, R.H. Bube, L. Gulbrandsen, W.Jansen, and P. Luscher, *J. Vac. Sci. Technol.* **A1**, 1469(1983).
12. A.J. Ricco, H.S. White, and M.S. Wrighton, *J. Vac.*

Sci. Technol. **A2**, 910(1984).

13. T.L. Chu, S.S. Chu, and S.T. Ang, *J. Appl. Phys*, **58**, 3206(1985).
14. F.A. Fonce, R. Sinclair, and R.H. Bube, *Appl. Phys. Lett.* **39**, 951(1981).
15. U. Solzbach and H.J. Richter, *Surf. Sci.* **97**, 191(1980).
16. J.A. Silberman, D. Laser, I. Lindau, W.E. Spicer, and J.A. Wilson, *J. Vac. Sci. Technol.* **B2**, 589(1984).
17. D.E. Aspenes and H. Arwin, *J. Vac. Sci. Technol.* **A 2**, 1309(1984).
18. H. Arwin and D.E. Aspenes, *J. Vac. Sci. Technol*, **A 2**, 1317(1984).
19. D.R. Rhiger and R.E. Kvass, *J. Vac. Sci. technol.* **21**, 168(1982); *J. Vac. Sci. Technol.* **19**, 472(1981).
20. G.D. Davis, T.S. Sun, S.P. Buchner, and N.E. Byer, *J. Vac. Sci. Technol.* **19**, 472(1981).
21. H. Neff, K.Y. Lay, B. Abid, P. Lange, K.J. Bachman, and G. Lucovsky, *J. Appl Phys.* **60**(1), 151(1986).
22. C.D. Wager, W.M. Riggs, L.E. Davis, J.M. Mulder, Handbook of X-ray Phhotoelectron spectroscopy, edited by G.E. Mullenberg(Perkin-Elmer Corporation, Eden Prire, Minnesota, 1978).