Fermi Level Stabilization Energy in Cadmium Oxide

D. T. Speaks^{1,2}, M. A. Mayer^{1,2}, K. M. Yu¹, S. S. Mao^{3,4}, E. E. Haller^{1,2} and W. Walukiewicz¹

¹*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

²*Department of Materials Science & Engineering, University of California at Berkeley, Berkeley California 94704, USA*

³*Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

⁴*Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California 94704, USA*

ABSTRACT

We have studied the effects of high concentrations of native point defects on the electrical and optical properties of CdO. The defects were introduced by irradiation with high energy He⁺, Ne⁺, Ar⁺ and C⁺ ions. Increasing the irradiation damage with particles heavier than He⁺ increases the electron concentration until a saturation level of $5 \times 10^{20} \text{ cm}^{-3}$ is reached. In contrast, due to the ionic character and hence strong dynamic annealing of CdO, irradiation with much lighter He⁺ stabilizes the electron concentration at a much lower level of $1.7 \times 10^{20} \text{ cm}^{-3}$. A large shift of the optical absorption edge with increasing electron concentration in irradiated samples is explained by the Burstein-Moss shift corrected for electron-electron and electron-ion interactions. The saturation of the electron concentration and the optical absorption edge energy are consistent with a defect induced stabilization of the Fermi energy at 1 eV above the conduction band edge. The result is in a good agreement with previously determined Fermi level pinning energies on CdO surfaces. The results indicate that CdO shares many similarities with InN, as both materials exhibit extremely large electron affinities and an unprecedented propensity for n-type conductivity.

I. INTRODUCTION

There has been increasing interest in group II-oxides, a class of semiconductors analogous to the very extensively studied and commercially successful group-III nitrides. ZnO has been thoroughly investigated but less attention has been paid to other group-II oxides. Although CdO has been synthesized by different methods, its properties are not very well established^{1 2 3 4 5 6}. There is still controversy regarding the nature, direct or indirect, of the fundamental band gap of this material. Recent angle-resolved photoemission spectroscopy (ARPES) studies have shown that the Fermi energy on the free CdO surface is pinned at about 1.15 eV above the conduction band edge (E_C)⁷. This resembles the extensively studied case of InN where the Fermi energy was found to be pinned deeply in the conduction band at $E_C+0.9$ eV. It is important to note that, as in InN, the surface Fermi level pinning energy for semiconductors is expected to be the same as the bulk Fermi level stabilization energy in heavily damaged materials^{8 9}. This important result is a consequence of the amphoteric defect model, originally developed for GaAs in the late 1980's, which has since been successfully applied to many other semiconductors^{8 9 10 11}. It was shown that the nature, donor or acceptor, of the native defects in semiconductors is determined by the position of the Fermi energy (E_F) with respect to the Fermi level stabilization energy (E_{FS}). The dominant native defects in a semiconductor are donors (acceptors) if $E_F < E_{FS}$ ($E_F > E_{FS}$). E_F stabilizes when the formation rates of both donors and acceptors are equal, and this occurs when $E_F = E_{FS}$. It should be noted that it has been shown in the case of GaAs for $E_F < E_{FS}$ ($E_F > E_{FS}$) both cation and anion site vacancies are donors (acceptors). Particle irradiation has been used previously in InN and other materials to effectively control the electronic properties¹²

because ions produce a uniform distribution of point defects where the defects tend to be acceptors or donors depending on the position of E_F relative to E_{FS} .

In a striking contrast to the surface pinning at $E_F=1$ eV in CdO determined by ARPES⁷, a recent study has shown that an intentional introduction of native point defects using irradiation with 1 MeV He^+ ions led to stabilization of the bulk Fermi energy at about $E_C + 0.4$ eV in CdO ¹³ which is almost 3 times lower than the surface Fermi level pinning energy. To address this inconsistency in the bulk and surface pinning of the Fermi level and to better understand the properties of native defects in CdO, we have performed systematic studies of electrical and optical properties of CdO irradiated with high energy ions of different mass and energy. We show that the irradiation-induced pinning energy depends on the damage introduction rate. A good agreement between surface Fermi level pinning and bulk Fermi level stabilization energy is achieved for high introduction rate of damage using heavy ions such as Ne and Ar that eliminates damage self-healing effects.

II. EXPERIMENTAL DETAILS

CdO films were deposited by pulsed laser deposition (PLD) on c-plane sapphire substrates. A Lambda Physik KrF excimer pulsed laser operating at 248 nm with a pulse width of 10 nanoseconds, energy fluence of 160 mJ and repetition rate of 5Hz was used. Sapphire substrates, 6 mm by 6 mm, were first cleaned with acetone followed by methanol. After mounting in the chamber, the substrates were baked at 500°C for 30 minutes to remove any residual contamination. A distance of 6 cm was maintained between the substrate and the pure Cd target during deposition. The films were deposited at 270°C with 40,000 laser pulses. Prior to deposition, the chamber was pumped down to

1×10^{-6} torr. During deposition the background pressure was maintained at a constant 4.2×10^{-4} torr by flowing O_2 .

The crystalline structure of the films was determined by X-ray diffraction (XRD). Film stoichiometry and thickness were measured by Rutherford backscattering (RBS) using a 2 MeV He^+ ion beam. The optical absorption edges were measured using a Perkin-Elmer Lambda 950 Spectrophotometer. Electron concentrations and mobilities were determined by Hall Effect in the Van der Pauw configuration using an Ecopia HMS-3000 system with a 0.6 Tesla magnetic field.

In order to compare the degree of irradiation damage among several different ions, the displacement damage dose methodology developed by the Naval Research Laboratory was used^{14 15}. The displacement damage dose (D_d in units of MeV/g) is defined as the non-ionizing energy loss (NIEL) multiplied by the dose. The NIEL for different ions in CdO were modeled using the SRIM (the Stopping and Range of Ions in Matter) program¹⁶. Point defects in CdO films were generated by irradiating the sample with 120 keV Ne^+ , 33 keV C^+ , 80 keV Ar^+ and 2 MeV He^+ particles with displacement damage doses ranging from 9.3×10^{14} to 1.0×10^{17} MeV/g.

III. RESULTS

Figure 1 shows the XRD spectrum of a CdO film deposited on sapphire. Only the CdO (002) peak ($2\theta=38.32^\circ$) is observed together with the sapphire (0006) substrate peak ($2\theta=41.70^\circ$). This suggests that the CdO film grows in the 00l preferred direction. The preferred growth direction is also confirmed by channeling RBS measurements that show a channeling yield $\chi \sim 0.5$. This preferred growth direction is expected because it is the

highest density plane and thus should have the lowest surface energy¹. The narrow (002) diffraction peak from the CdO also indicates a large grain size. Using the Scherrer equation, the grain size is found to be on the order of 150 nm. This is on the same order of film thickness as measured by RBS, i.e. 130 nm.

Hall Effect measurements show that the as-grown film is n-type with an electron concentration of $9 \times 10^{19} \text{ cm}^{-3}$ and mobility of $89 \text{ cm}^2/\text{V-s}$. Due to the large electron affinity of the material, CdO films have a clear tendency to be n-type. In fact, all reported CdO films are n-type with electron concentration on the order of 10^{19} - $10^{20}/\text{cm}^3$. The mobility of $89 \text{ cm}^2/\text{V-s}$ measured in our film is higher than most CdO thin films reported in the literature with comparable electron concentration. The XRD, RBS and electrical measurements indicate that the quality of these as-grown CdO films is rather high.

The XRD spectrum of the CdO irradiated by 120 keV Ne^+ ions to a total fluence of $1.2 \times 10^{14} \text{ cm}^{-2}$ (corresponding to a $D_d \sim 6.7 \times 10^{16} \text{ MeV/g}$) is also shown in Figure 1. We note that this irradiation condition gives rise to saturation of electrical properties in CdO. First we observe that the high irradiation dose does not amorphize the film as the (002) diffraction peak is still present, though slightly shifted to a lower value. This suggests that the point defects created by Ne irradiation result in an increase of the lattice constant, a behavior also observed in InN^9 .

The effect of irradiation on the electron concentration is shown in Figure 2. For comparison, irradiation effects in InN and the recent reported results by King et al. on CdO are also shown¹³. Similar to the case of InN, irradiation increases the free carrier concentrations in all CdO films. Regardless of the ion used, saturation of the electron

concentration is observed for CdO as the displacement damage dose increases to $>2 \times 10^{16}$ MeV/g. These results are consistent with the amphoteric defect model (ADM)⁸ assuming that the Fermi level stabilization energy, E_{FS} in CdO lies well above the conduction band minimum. Therefore, the irradiation-induced point defects are predominantly donors leading to an increase of the electron concentration and an upward shift of the Fermi energy, E_F towards E_{FS} . For $E_F = E_{FS}$, introduction of new defects does not change the electron concentration or the Fermi energy as the formation rates of donor- and acceptor-like defects are equal.

Results in Figure 2 show that the irradiation with C^+ , Ne^+ and Ar^+ ions leads to an increase in electron concentration and the eventual saturation of the electron concentration at $N_{sat} \sim 4.5-5.0 \times 10^{20} \text{ cm}^{-3}$ with the damage doses $D_d > 2 \times 10^{16} \text{ MeV/g}$. Electron concentration is related to the Fermi level according to

$$n = \frac{1}{3\pi^2} \int_{E_C/k_B T}^{\infty} \frac{\exp\left(z - E_F/k_B T\right)}{1 + \exp\left(z - E_F/k_B T\right)} k^3(z) dz \quad (1)$$

where k_B is the Boltzmann constant, $z = E_C/k_B T$, E_F is the electron energy and E_C is the energy of the conduction band edge. The nonparabolic dispersion relation for CdO was derived from Kane's two band $\mathbf{k}^* \mathbf{p}$ model¹⁷:

$$E_c(k) = \frac{\hbar^2 k^2}{2m_0} - \frac{E_g}{2} + \sqrt{\left(\frac{E_g}{2}\right)^2 + \left(\frac{E_g \hbar^2 k^2}{2m_0^*}\right)} \quad (2)$$

The carrier concentration as a function of Fermi energy, E_F , is calculated using Eq. 1 with k dependence on E obtained by solving Eq 2. Assuming the conduction band edge electron effective mass of $m_0^* = 0.21m_0$ we find that the saturation electron concentration $N_{sat} \sim 5 \times 10^{20} \text{ cm}^{-3}$ corresponds to E_F , and thus also E_{FS} , located deeply in the conduction

band at $\sim E_C + 1$ eV. This location of E_{FS} is in a good agreement with the recently reported surface level pinning energy measured by photoelectron spectroscopy⁷. These results confirm the basic assertion of the ADM that the same mechanism is responsible for the Fermi level pinning on the surface and the Fermi level stabilization in the bulk of CdO. Our heavy particle irradiation experiments point to certain similarity of the defect behavior in CdO and InN⁹. In both instances damage produces high concentration n-type material with E_{FS} located almost 1 eV above the conduction band edge. This is in a stark contrast with most semiconductors where E_{FS} is located in the band gap and irradiation produces high resistivity material.

Interestingly, the results in Figure 2 show a large difference in the dependence of the saturation electron concentration on the damage produced by a heavy ion and He^+ irradiation. In our He^+ irradiated sample the electron concentration saturates at about $1.7 \times 10^{20} \text{ cm}^{-3}$. This is very close to the electron concentration saturation of $2 \times 10^{20} \text{ cm}^{-3}$ reported by King et al.¹³ for CdO irradiated with 1 MeV He^+ ions but much lower than the N_{sat} obtained with the heavy ion irradiation. In contrast to CdO, irradiation of InN with 2 MeV He^+ , as well as with Ne^+ , stabilizes the Fermi level at $E_C + 0.9$ eV, the same as Fermi level pinning position on InN surfaces. A likely cause of this discrepancy in the value of N_{sat} obtained from He and heavy ion irradiation in CdO is the large difference in the damage production rate for these ions. We note that the NIEL of a 120 keV Ne^+ ion in CdO is over 500 times higher than that of a 2 MeV He^+ ion. This means that for similar irradiation currents, the defect production rate in CdO for a heavy ion (Ne^+ , C^+ , Ar^+) is at least 2 orders of magnitude higher than for much lighter He ions. Therefore, irradiation with heavy ions produces a high density of vacancies and interstitials in the

ion path. Fast diffusing interstitials form stable clusters that act as sinks for newly formed interstitials leaving the vacancies which, as has been discussed in the introduction, are expected to be electrically active donors for $E_F < E_{FS}$ and stabilize the Fermi energy at E_{FS} . In the case of He^+ irradiation, the lower density of defects in the path of the high energy ion prevents precipitation of interstitials that remain isolated in the crystal lattice. Subsequently produced vacancies have a large chance to be annihilated by these interstitials. At high enough irradiation doses, a balance between production and annihilation of the vacancies is established resulting in saturation of the electron concentration and stabilization of the Fermi energy below E_{FS} . Dynamic annealing becomes much more significant for more ionic materials such as CdO. This empirical relationship between bond ionicity and degree of dynamic annealing has been known since the 1970s', however the exact physical mechanisms that cause this phenomena are not well established^{18 19}. However, Kucheyev states that the two most likely mechanisms are an increase in electrostatic energy associated with substitutional disorder and electrostatically lowering energy barriers for defect interaction processes as ionicity increases²⁰. What is known is that very ionic materials, such as ZnO, exhibit strong dynamic annealing, and ZnO and CdO have comparable ionicity²¹. In addition, similar dynamic annealing behavior has been recently observed in Zr-irradiated pure and yttria-stabilized zirconia²² where dynamic annealing was found to be especially significant in the presence of oxygen vacancies, a condition that is also present in CdO.

In order to further evaluate effects of irradiation on the properties of CdO, we have measured optical properties and analyzed the electron concentration-dependent position of the optical absorption edge in terms of the Burstein-Moss shift²³. Figure 3

shows the optical absorption curves for the same CdO thin film which was sequentially irradiated with increasing Ne^+ ion dose.

A clear blue shift in the absorption edge is observed with increasing irradiation dose. Notice that the initially small increases in irradiation dose result in large shifts in the position of the absorption edge. However, as the dose approaches the saturation level the shift in the absorption curves becomes smaller until almost no movement in the absorption edge is observed even for doubling the irradiation dose. The absorption edge shift to higher energy is well described by the Burstein-Moss shift: electrons filling the bottom of the conduction band result in a blue shift in the optical absorption edge energy due to the Fermi exclusion principle. This is depicted qualitatively in Figure 4a: the red line (labeled E_F) represents the Fermi level above the conduction band minimum. As the Fermi level moves higher in the conduction band with the addition of electrons, it eventually stabilizes at E_{FS} represented by the solid green line in Figure 4a.

To quantify this shift, we compare the experimental data with calculated absorption edges using the CdO band structure in conjunction with E_F values directly deduced from Hall effect electron concentrations. Because of the large electron concentrations, the position of the conduction band edge and also the Burstein-Moss shift are expected to be affected by electron-electron and electron-ion interactions. First, the experimental edge was extracted for each data curve shown in Figure 3 by fitting with an analytical expression because a standard α^2 linear approximation does not necessarily apply in a complex case²⁴. A standard absorption expression for optical absorption was convoluted with a Gaussian curve to account for experimental broadening of the absorption edge:

$$\alpha(E') = \int_{-\infty}^{\infty} A(E - E_{AE})^{1/2} \frac{\exp - \left(\frac{(E' - E)^2}{\Delta} \right)}{\Delta \sqrt{\pi}} dE \quad (3)$$

where A is a scaling factor and Δ is the broadening parameter. For each curve, the value of the energy absorption edge, E_{AE} labeled as “Optical Absorption at k_F ” in Figure 4a was determined from fitting Eq. 3 to the experimental data shown in Figure 3. With values of Δ of 0.3eV or less, we were able to obtain good fits to the first 6 absorption curves and extract the absorption edges shown as solid circle symbols in Figure 4b.

It is important to note that the Fermi level calculated from the Hall Effect electron concentration using Eq. 1 is measured from the bottom of the conduction band. However, because the absorption edge is measured with respect to the valence band, the shift in the conduction band edge and the curvature of the valence band are included in order to compare the Fermi levels extracted from the Hall effect to those from the absorption data. In an n-type semiconductor, the conduction band shifts because of the electron-electron and electron-ion interaction. Therefore the corrected absorption edge energy represented by blue line in Figure 4a can be expressed as:

$$E_{AE}(E, n) = E_{Gap} + E_{F-Hall}(n) - E_{Ie-e}(n) - E_{Ie-i}(n) + \frac{(\hbar k(n)^2)}{2m_{hole}} \quad (4)$$

where E_{Gap} is the direct band gap of 2.16, E_{F-Hall} is the Fermi level calculated from Hall effect measurements, and $E_{Ie-e}(n)$ is the electron-electron (e-e) interaction calculated according to^{25 26}:

$$E_{Ie-e} = -\frac{2e^2 k_F}{\pi \epsilon_o} - \frac{e^2 \lambda}{2\epsilon_o} \left[1 - \frac{4}{\pi} \tan^{-1} \left(\frac{k_F}{\lambda} \right) \right] \quad (5)$$

where $k_F=(3\pi^2n)^{1/3}$ is the Fermi wave vector, n is the carrier concentration, λ is the Thomas Fermi screening parameter and is given by the following equation

$$\lambda = 2x \left(\frac{k_F}{\pi a_B} \right)^{1/2} \quad (6)$$

where a_B is the Bohr radius. $E_{I_{e-i}}(n)$ is the electron-ion (e-i) interaction calculated according to ^{25 26}

$$E_{I_{e-i}} = -\frac{4\pi m e^2}{\epsilon_o a_o \lambda^3} = -\frac{e\hbar}{2} \left[\frac{\pi^3 n}{\epsilon_o m^*} \right]^{1/2} \quad (7)$$

The last term in Eq. 4 accounts for an assumed parabolic dispersion relation of the valence band. The contributions of different terms in Eq. 4 are schematically shown in Figure 4a. As shown by the dashed curve, both the e-e and e-i interactions shift the conduction band down. The Hall electron concentration defines the position of the Fermi energy E_F relative to the shifted conduction band edge. On the other hand, for a given electron concentration the optical absorption edge energy is reduced by e-e and e-i interactions. The sum of $I_{e-i}(n)$ and $I_{e-e}(n)$ terms ranges from 0.1 eV in the low concentration to 0.3 eV in the highest concentration samples. The dashed lines in Figure 4b represent the electron concentration dependence of the absorption edge calculated using Eq. 4 with several values of the hole effective masses. It is seen that the absorption edge energy calculated for the hole effective mass larger than $2m_0$ agrees very well with experiment.

As seen in Figure 4b, the shift of the absorption edge energy saturates at approximately 3.0 eV, corresponding to the electron concentration of about $5 \times 10^{20} \text{ cm}^{-3}$. The saturation energy represents the position of the Fermi level stabilization energy (E_{FS})

at this high electron concentration. In order to determine E_{FS} in intrinsic CdO, we note that both the e-e and e-i interactions shift the conduction band downward whereas E_{FS} is affected only by the electrostatic potential of the e-i interaction. Consequently, as is shown in Figure 4a, the extrapolation to a negligible electron concentration locates E_{FS} at 3.16 eV above the valence band edge or at 1.0 eV above the conduction band edge. This location of E_{FS} is in good agreement with the pinning of the Fermi energy on the CdO surface as determined in a recent angle-resolved photoelectron spectroscopy (ARPES) experiment⁷. From the known location of the E_{FS} at 4.9 eV below the vacuum level one obtains the value of 5.94 eV for the electron affinity of CdO. This large electron affinity explains the extreme propensity of CdO for n-type conductivity and points at great similarity between properties of CdO and previously extensively studied InN⁹.

IV. CONCLUSIONS

In conclusion, we introduced point defects into high quality CdO thin films deposited by pulsed laser deposition by ion irradiation. We found that the carrier concentration increases as irradiation fluence increases and finally saturates at $5 \times 10^{20} \text{ cm}^{-3}$. At the same time, we also observe that the optical absorption edge increases from 2.4 eV for the as grown film to 3.0 eV above the valence band in the most heavily irradiated samples. The increase in the optical absorption edge energy is attributed to the Burstein-Moss shift. We show that the saturation of the electron concentration and the absorption edge energy can be accounted for by stabilization of the Fermi energy at E_{FS} located at ~ 1.0 eV above the conduction band minimum. The discrepancy between He^+

and heavy ion irradiation in CdO can be explained by the large damage production rate difference between different ions and the strong ionic character of CdO.

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FIGURE CAPTIONS

Figure 1. (Color online) X-ray diffraction of as grown and Ne irradiated CdO on sapphire.

Figure 2. (Color online) Electron concentrations in CdO as a function of displacement damage dose using several different ions.

Figure 3. (Color online) Optical absorption edge of Ne irradiated CdO.

Figure 4. (Color online) a) Schematic defining the measured optical absorption edge, original band gap and effects of electronic interactions. b) Measured optical absorption edge compared with E_F values determined from Hall effect measurements and calculated absorption edges including electron-electron interaction and assuming different electron effective masses. The Fermi level stabilization energy of about at 3.16 eV above the valence band is obtained for both sets of measurements.

Figure 1

Figure 2

Figure 3

Figure 4