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Characterization of cubic phase MgZnO/Si(1 0 0) interfaces

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Abstract

The microstructural properties of the $Mg_xZn_{1-x}O$/Si(1 0 0) interface were investigated using transmission electron microscopy (TEM) and chemical states of the heterostructure were studied by high resolution X-ray photoelectron spectroscopy (XPS). By analyzing the valence band spectra of thin $Mg_xZn_{1-x}O$/Si(1 0 0) heterostructures, the valence band offset between such $Mg_{0.55}Zn_{0.45}O$ and Si(1 0 0) was obtained to be 2.3 eV. Using the cubic ternary thin films as insulators, metal–insulator–semiconductor (MIS) capacitors have been fabricated. Leakage current density lower than 3×10^{-7} A/cm^2 is obtained under the electrical field of 600 kV/cm by current–voltage (*I*–*V*) measurement. Frenkel-Poole conduction mechanism is the main cause of current leakage under high electrical field.
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Keywords: MgZnO thin film; Band offset; MIS structure; Leakage mechanism

1. Introduction

The continued scaling down of complementary metal-oxide semiconductor (CMOS) technology is pushing the thickness of SiO_2 towards 1 nm as the gate dielectric. Owing to its unacceptable tunneling leakage current and intrinsic reliability concerns, SiO_2 is reaching its physical limit. Alternative gate dielectrics are very desirable to meet the technological requirement of CMOS. Utilizing an insulator with a higher dielectric constant than that of SiO_2 (i.e., a high-*k* dielectric) enables the use of a larger physical thickness to maintain the same capacitance. In the recent years, there has been much interest in the zinc oxide (ZnO) materials and fabrication of ZnO-related heterostructures. Novel cubic $Mg_xZn_{1-x}O$ ($x \geq 0.50$) epitaxial heterostructures on Si(1 0 0) substrates were synthesized by pulsed laser deposition (PLD) [1] and reactive electron beam evaporation deposition (REBED) at low growth temperature [2]. Optical properties including wide band gap ($E_g > 5.0$ eV) were reported previously [3]. The temperature-

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dependent bandgaps of the cubic phase $Mg_xZn_{1-x}O$ films have been measured by ultraviolet optical transmission with temperature variation from 10 to 300 K and analyzed by theoretical simulating the optical absorption spectra [4]. Indices of refraction for cubic phase $Mg_xZn_{1-x}O$ ($0.57 \leq x \leq 1$) thin film alloys were obtained to be between 1.89 and 1.70 by transmission spectra and Manifacier method [5]. The electrical properties including high dielectric constant ($\varepsilon \sim 10.5$) and low leakage current were attended [3]. These properties of the new material are rendering new applications such as application in micro- and nano-electronic devices [6,7].

As a candidate of high-*k* material for dielectric oxides, the interface in direct contact with channel region in MOS must be engineered to permit low interface trap density (e.g. dangling bonds) and minimize carrier scattering (maximize mobility in the channel) in order to obtain reliable and high performance. Another crucial requirement for high-*k* material is low leakage currents. It is desirable to find a gate dielectric that has large ΔE_c value to Si, the conduction band offset, and perhaps to other gate metals which may be used. If the experimental ΔE_c values for these oxides are even much less than 1.0 eV, it will likely preclude the applications of these oxides as gate dielectrics because electron transport (either by thermal emission or tunneling) would lead to unacceptably high leakage currents [8]. The values $\Delta E_c \sim 2.3$–2.8 eV for Al_2O_3 and Y_2O_3, and $\Delta E_c \sim 1.5$ eV for ZrO_2 and $ZrSiO_4$ were reported by Roberson [9].

In this report, we use X-ray photoelectron spectroscopy (XPS) to demonstrate the conduction band offset ΔE_c of cubic phase MgZnO epitaxial layer to Si. Using the cubic ternary thin films as insulators, metal–insulator–semiconductor (MIS) capacitor structures have been fabricated. Current–voltage (*I*–*V*) characteristics were analyzed to explore the leakage mechanism in the film under high electrical field.

2. Experiment

Cubic phase $Mg_xZn_{1-x}O$ ($x > 0.5$) layers were deposited by a reactive e-beam evaporation system on *p*-type Si(100) wafers with a resistivity of 1–5 Ω cm. Since Si wafers usually have an ultra thin native SiO_x layer of 1–5 nm on top of the Si substrate, a 0.5% HF strip of the surface chemical oxide was followed by pure water rinse to eliminate residual Si–F bonds prior to the deposition of $Mg_xZn_{1-x}O$ dielectric layer. The $Mg_xZn_{1-x}O$ layers were deposited at 250 °C in oxidation ambient with chamber pressure of 2×10^{-4} Torr. The details of growth of cubic phase $Mg_xZn_{1-x}O$ thin film and the determination of Mg composition were published in the references [3,5]. The thicknesses of the $Mg_xZn_{1-x}O$ dielectric layers varied between 80 and 300 nm measured by Taylor-Hobson Talystep.

To characterize chemical and electronic structure of the films, high-resolution XPS was carried out utilizing monochromatized Al Kα (1486.6 eV) radiation by Perkin-Elmer PHI 5000C ESCA System. The core levels such as Si_{2p}, Mg_{2p} and Zn_{2p}, and the valence band spectra of the samples were taken at photoelectron take-off angles of 45° and 90°. To fabricate MOS capacitors, 300 nm Al layer was deposited on $Mg_xZn_{1-x}O$ and then 450 °C rapid thermal processing (RTP) treatment for Ohm contact was preceded. MOS capacitors were defined on the gate dielectric stacks by lithography through a shadow mask with a capacitor area of 0.15 mm^2. The oxide leakage current characteristics were measured using HP 4156 Precision Semiconductor Parameter Analyzer.

3. Results and discussion

3.1. Micro-structural features at interface of MgZnO/Si(1 0 0)

Fig. 1 (a) shows cross-section TEM micrograph from a sample of $Mg_{0.55}Zn_{0.45}O$ thin film deposited on Si(1 0 0) substrate. The cross-section micrograph clearly shows the interface between the Si substrate and $Mg_{0.55}Zn_{0.45}O$ epitaxial layer, which exhibits a polycrystalline structure. The magnified grain configuration is shown in the inset. We note that the size of crystal grains is about tens nanometer. Similar images are observed along the interface between the epitaxial layer and Si substrate. In Fig. 1(b), we show micro-diffraction patterns from the epitaxial layer. From these diffraction studies, it is clearly evident that the synthesized $Mg_{0.55}Zn_{0.45}O$ films possess cubic symmetry with cube-on-cube alignment. This is consistent

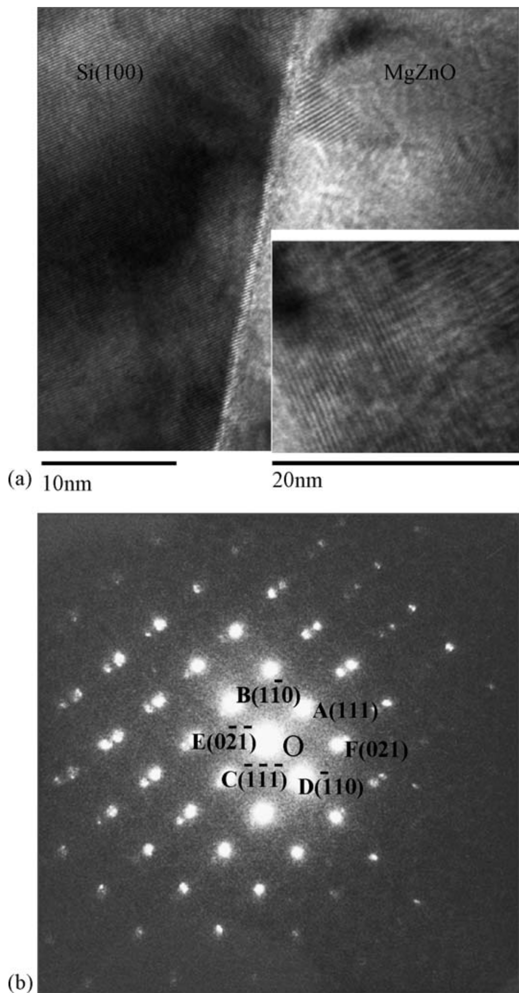

Fig. 1. (a) FE-TEM images of cubic $Mg_{0.55}Zn_{0.45}O$ by REES methods and inset is the detail of cubic crystal grain region. (b) The micro-diffraction patterns of the cubic $Mg_{0.55}Zn_{0.45}O$ film.

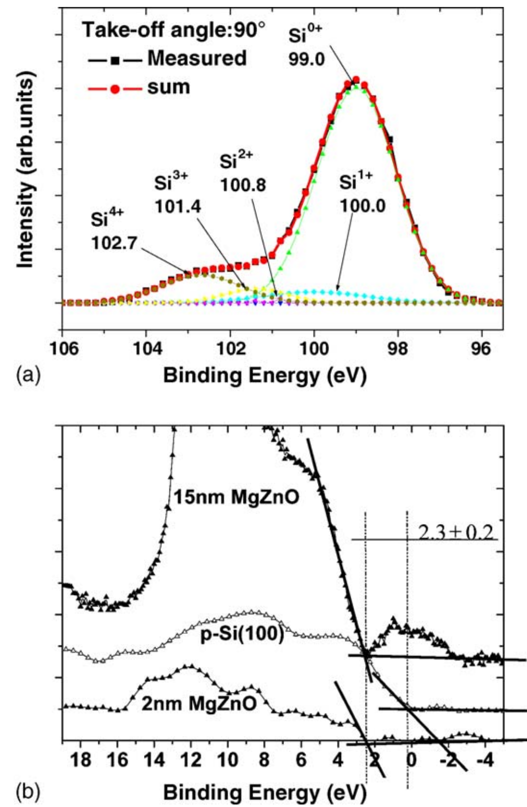

Fig. 2. (a) Si 2p XPS spectrum is measured at the take-off angle of 90° (fine solid line) and the components of Si substrate (Si^{0}) and suboxides (Si^{1+}–Si^{4+}) are denoted; (b) O1s XPS spectrum.

with X-ray diffraction of high (1 0 0) orientation. The couple highlight points represent the overlap crystal grain.

To investigate the characteristics of interface between the oxide and silicon substrate, XPS characterization was performed. Fig. 2(a) shows Si 2p spectra taken from the sample with 2 nm thick $Mg_{0.55}Zn_{0.45}O$ on Si(1 0 0). The measured Si 2p spectrum can be represented by summing the spectra of various oxidation states. To investigate the oxidation states more quantitatively, we fitted the spectra using a standard curve-fitting procedure provided by the XPS manufacturer. The fully oxidized states of Si atoms shown in the Fig. 2(a) are Si^{4+} in the SiO_2 thin film, bulk states in the substrate are Si^{0+}, and intermediate oxidation states Si^{1+}, Si^{2+}, Si^{3+} in the transition layer [10]. It is seen that the states of Si^{0+} dominate the spectrum and the density of intermediate oxidation states (Si^{1+}, Si^{2+}, Si^{3+}) is small. From Fig. 2, it is seen that the energy shift of Si^{4+} component from the substrate component (Si^{0+}) is 3.7 eV, which has a good fit to the measured spectrum. It indicates that silicon dioxide with Si binding energy of 102.7 eV are almost completely formed at the interface. The density of Si^{2+} component with chemical shift from Si^{0+}, being 1.8 eV, is smallest. The XPS signal intensity ratio of bulk silicon and the oxide components are Si^{0+}:Si^{1+}:Si^{2+}:Si^{3+}:Si^{4+} = 573:35:1:30:73.

As shown in the Fig. 2(b), the O1s XPS spectrum shows a single peak at 531 eV. Signal of Si–O bond at 532 eV is not observed. However, Miyazaki observed

strong Si–O signal of 532 eV at the interface of ZrO_2/Si(1 0 0) with the formation of interfacial oxide layer as thin as 1.7 nm, by 500 °C annealing in dry O_2 for 5 min [11]. Therefore, it can be concluded that the silicon oxides at the interface is in monolayer scale because the $Mg_{0.55}Zn_{0.45}O$ layer on Si was grown at low temperature. Fig. 3(a and b) shows Mg 2p and Zn 2p spectra. The Mg 2p shifts positive 0.6 eV from the Mg 2p (MgO) with binding energy of 50.80 eV, while the Zn 2p shifts negative 0.6 eV from the Zn 2p (ZnO) with binding energy of 1021.75 eV. The shift of binding energy could be related to the formation of ternary MgZnO alloy film.

For thin gate dielectrics, the interface with Si plays a key role and in most cases is a dominant factor in determining the overall electrical properties. Thermodynamic stability of the MgZnO/Si(1 0 0) interface is an important issue. A comprehensive investigation of the thermodynamic stability of binary oxides in contact with silicon was conducted by Schlom et al. [12]. It was concluded that MgO is thermodynamically stable in contact with silicon at 1000 K, while Zn–O bonds are not stable in contact with Si at such a high temperature [13]. Our previous Auger electron spectrometry (AES) depth profiles for the as-grown MgZnO films (with growth temperature of 250 °C) demonstrated good uniformity of Mg, Zn and O components over 60 nm film thickness [14]. However, after high temperature (900 °C) annealing under O_2 ambient, distinct profile change of Zn concentration in the film and at interfacial region was observed. The changes of Zn profile indicate the breaking of Zn–O bonds in contact with Si and Zn migrating towards the surface at such high annealing temperature. In contrast, Mg component profile was still uniformly distributed after the MgZnO films were annealed at 900 °C under O_2 ambient, indicating MgO is stable at such a high annealing temperature [14]. These AES observations are consistent with Schlom's results.

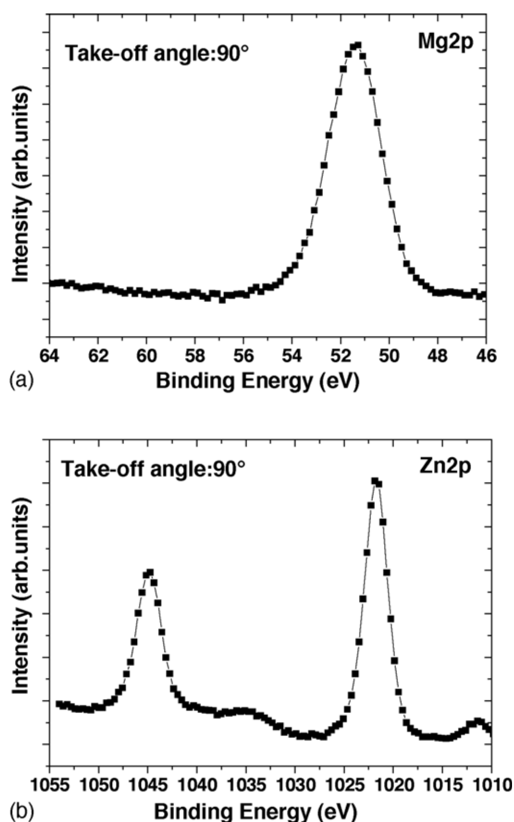

Fig. 3. XPS spectra of 2 nm thick $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0): (a) Mg 2p; (b) Zn 2p.

3.2. Analysis of valence band spectra and determination of energy band alignments

To obtain the valence band offset of $Mg_{0.55}Zn_{0.45}O$/Si heterostructure, valence band spectra was measured by low energy XPS. Two $Mg_{0.55}Zn_{0.45}O$/Si heterostructure samples were prepared with $Mg_{0.55}Zn_{0.45}O$ film thicknesses of 2 and 15 nm. Fig. 4(a) shows the valence band spectrum for $Mg_{0.55}Zn_{0.45}O$ (2 nm)/Si(1 0 0) heterostructure and reference spectrum measured from Si(1 0 0) substrate. Then the spectrum for $Mg_{0.55}Zn_{0.45}O$ film was obtained by subtracting the reference spectrum of Si(1 0 0) substrate from the measured spectrum for $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0) heterostructure. Fig. 4(b) shows the valence band photoelectron energy-distribution curves for the two $Mg_{0.55}Zn_{0.45}O$ coverages (2 and 15 nm) and for Si(1 0 0) substrate. The binding energy of each valence band spectrum was calibrated by the energy position of the corresponding C 1s peak of the surface and Si 2p of the Si(1 0 0) substrate. For 15 nm thick $Mg_{0.55}Zn_{0.45}O$ film in which XPS signal from Si(1 0 0) substrate could not be detected, the binding energy of Zn 3d peak (10.7 eV) in Fig. 4(b) was referred to see the valance band edge of $Mg_{0.55}Zn_{0.45}O$. Notice that the leading edges of valence-band for the two samples are clearly seen. A

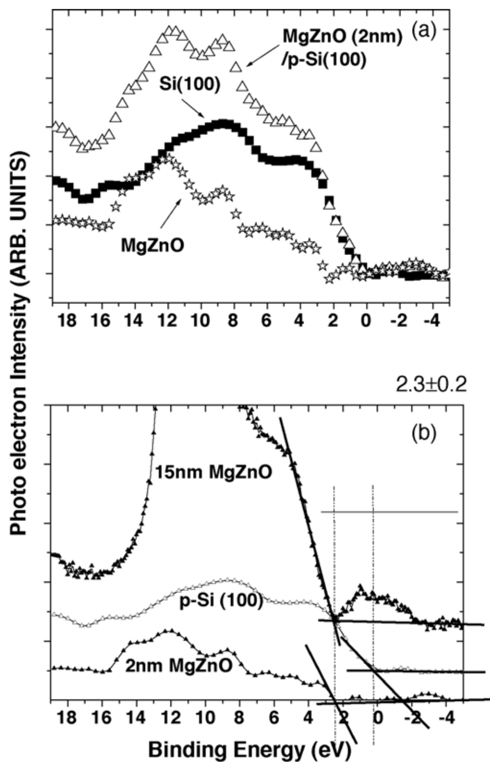

Fig. 4. (a) The measured valence band spectrum for $Mg_{0.55}Zn_{0.45}O$ (2 nm)/Si(1 0 0) heterostructure and reference spectrum measured from Si(1 0 0) substrate; (b) the detail diagrammatic curve for the valence band offset ΔE_v of the cubic $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0) heterostructure.

direct measurement of valence band offset (ΔE_v) of $Mg_{0.55}Zn_{0.45}O$/Si heterostructure is possible in this case by linear extrapolation of the two edges [9]. The edge positions deduced by linear extrapolation were cross-checked for different systems with those deduced from the energy positions of the corresponding core levels. As a result, the valence band offset ΔE_v at the interface of $Mg_{0.55}Zn_{0.45}O$/Si heterostructure is 2.30 eV. Considering the band gap energies of $Mg_{0.55}Zn_{0.45}O$ (5.76 eV) [3] and Si (1.12 eV), as shown in the Fig. 5, the conduction band offset ΔE_c is obtained to be 2.34 eV.

3.3. Leakage current and conduction mechanism

The Al/$Mg_{0.55}Zn_{0.45}O$ (80 nm)/p-Si/Al MIS structures were fabricated with 0.15 mm^2 area of Al electrode on both of $Mg_{0.55}Zn_{0.45}O$ surface and silicon

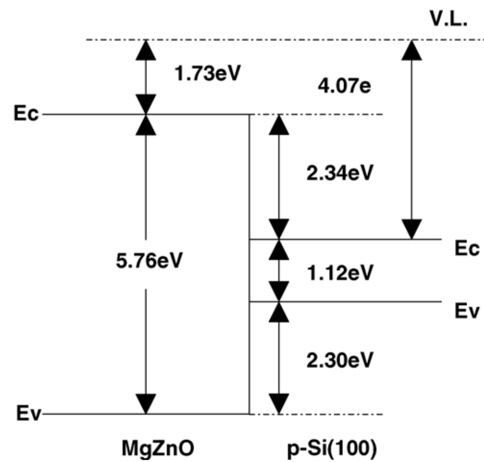

Fig. 5. Energy band profile for cubic $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0) heterostructure.

substrate. Then it was annealed at 450 °C in N_2 atmosphere. The corresponding current–voltage (*I–V*) characteristic for the MIS structure is shown in Fig. 6. The leakage current density is as low as 3×10^{-7} A/cm^2 at the bias of 5 V (electrical field of ~600 kV/cm). In contrast, similar MIS structure which is made of 65 nm thick SiO_2 layer as insulator has leakage current of approximately 4×10^{-4} A/cm^2, nearly three orders of magnitude higher than that of the $Mg_{0.55}Zn_{0.45}O$ insulator devices. The measured leakage current at room temperature consists of three different conduction mechanisms including Ohm current, Fowler-Nordheim (F-N) tunneling current

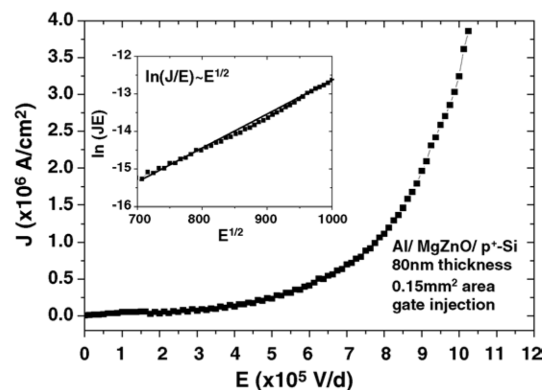

Fig. 6. Leakage current density vs. electrical field for the Al/$Mg_{0.55}Zn_{0.45}O$/Si(1 0 0)/Al MIS structure. The inset is the fitting results of F-P conduction.

and Frenkel-Poole (F-P) current which is generated from the defects and electron traps in the insulators under the high electrical field. For the gate electron injection case, the gate insulating layer is under high electrical field. The F-P leakage current can be expressed in the following formula [15]:

$$J \sim E \exp(b\sqrt{E}) \quad (1)$$

where E is the electrical field and b is the constant at a temperature when the I–V curve was measured. As shown in the inset of Fig. 6, the calculation of F-P current is in good agreement with the measured I–V curve. Therefore, the observed I–V characteristic in $Mg_{0.55}Zn_{0.45}O$ MIS device shown in Fig. 6 follows high electrical field F-P conduction mechanism. It is worth noting that F-P conduction mechanism dominates over F-N tunneling current, a process whereby electrons tunnel through a barrier between the isolator and semiconductor in the presence of a high electric field, and the Schottky emission which is due to the lowering of potential barrier at the metal-semiconductor contact under high electric field. This means that the density of electrons in the trap and the trap energy in $Mg_{0.55}Zn_{0.45}O$ films is the main cause of leakage.

4. Conclusion

The cross-section image of TEM for the cubic $Mg_{0.55}Zn_{0.45}O$ films grown on Si(1 0 0) demonstrates clean interfacial boundary. From the XPS analysis of chemical bonding features near the interfaces of cubic $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0), silicon–oxygen bonding has not been observed, indicating that the silicon oxide transition layer can be in monolayer scale. This is attributed to the low growth temperature of $Mg_{0.55}Zn_{0.45}O$ on Si(1 0 0). The valence band offset of 2.30 eV between cubic $Mg_{0.55}Zn_{0.45}O$ and Si(1 0 0) is determined by analyzing the valence band spectra of thin $Mg_{0.55}Zn_{0.45}O$/Si(1 0 0) heterostructure. Using the cubic $Mg_{0.55}Zn_{0.45}O$ thin films as insulator, MIS structures have been fabricated. Leakage current density as low as 10^{-7} A/cm^2 is obtained at an electrical field of 600 kV/cm. The observed I–V characteristic in the $Mg_{0.55}Zn_{0.45}O$ MIS device follows high electrical field F-P conduction mechanism which indicates that the density of electrons in the trap and the trap energy in the $Mg_{0.55}Zn_{0.45}O$ film is the main cause of leakage.

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