Applications of Cubic MgZnO Thin Films in Metal–Insulator–Silicon Structures

2004 Chinese Phys. Lett. 21 1135

(http://iopscience.iop.org/0256-307X/21/6/044)

CHIN.PHYS.LETT. Vol. 21, No. 6 (2004) 1135

Applications of Cubic MgZnO Thin Films in Metal–Insulator–Silicon Structures *

LIANG Jun(梁军)[1], WU Hui-Zhen(吴惠桢)[1,2**], LAO Yan-Feng(劳燕锋)[1], QIU Dong-Jiang(邱东江)[2],
CHEN Nai-Bo(陈奶波)[2], XU Tian-Ning(徐天宁)[2]

[1]*State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050*
[2]*Department of Physics, Zhejiang University, Hangzhou 310027*

(Received 25 November 2003)

Cubic $Mg_{0.55}Zn_{0.45}O$ thin film alloys have been deposited on Si substrates at low growth temperature. The topography of the cross section of the epitaxial film by scanning electronic microscope demonstrates good morphology and high interfacial quality. The high (001) orientation and wide band-gap ($E_g > 5.5\,eV$) of the cubic $Mg_{0.55}Zn_{0.45}O$ thin films accord with the guidelines for metal–insulator–silicon (MIS) device applications. Using the cubic ternary thin films as insulators, MIS structures have been fabricated. The capacitance–voltage measurements show the flat band voltage shift V_{FB} of 11.8 V and mobile ion density D_{mc} of $5.57 \times 10^{10}\,cm^{-2}$ for the MIS structure. Leakage current density as low as $\sim 10^{-7}\,A/cm^2$ is obtained at $E = 700\,kV/cm$ by the current–voltage measurements. These unique structural and electrical properties of the fabricated MIS devices indicate that cubic MgZnO materials could become a new candidate for high-κ dielectrics used in silicon integrated circuit technologies.

PACS: 77.55.+f, 73.40.Qv, 73.61.−r

In the silicon based capacitance and complementary metal-oxide–semiconductor (CMOS) integrated circuit industry, the necessity of finding an alternative to SiO_2 as the gate material becomes imperative as device dimensions shrink towards the 0.1-μm range. At this channel length, oxide thickness should be in the order of 15–20 Å. Such ultra-thin oxides may not be usable for the manufacture of high performance CMOS circuits due to gate leakage current through the film and the effect of boron penetration from the polysilicon gate contact. High-k dielectrics are widely studied in order to suppress gate leakage current for the realization of scaled-down ULSI devices. For example, rare-earth metal oxides such as CeO_2,[1] HfO_2,[2,3] Y_2O_3,[4,5] and ZrO_2,[6] which exhibits a small equivalent oxide thickness (EOT) and small leakage current density have attracted much attention recently as alternative gate dielectrics. However, within the alternative candidates very few dielectrics are promising with respect to the guidelines for CMOS devices that require high permittivity, wide band gap, high interface quality and thermodynamic stability. The recently synthesized wide band gap, cubic MgZnO (having NaCl crystal structure), grown on silicon is possibly a new candidate for high-κ dielectrics used in silicon technologies.

Wide band gap ($E_g > 5.0\,eV$), cubic $Mg_xZn_{1-x}O$ ($x \geq 0.33$) thin-film alloys have recently been deposited on different substrates. In 2002, Choopun *et al.*[7] reported the realization of wide band gap (5–6 eV), cubic-phase $Mg_xZn_{1-x}O$ thin-film alloys grown on sapphire by pulsed laser deposition. The structural transition from hexagonal to cubic phase has been observed for Mg composition greater than 33 at.%. More recently, Qiu *et al.*[8] reported the successful growth of cubic $Mg_xZn_{1-x}O$ thin films on Si substrates by reactive electron beam evaporation at very low substrate temperature (200–250°C). X-ray diffraction showed that the cubic thin films deposited on Si are highly (001) oriented, in contrast to that being highly (111) oriented when grown on sapphire. Its optical absorption edge higher than 5.5 eV was observed from transmission measurements. These properties per se render reasonable applications for the high-κ gate oxide. However, the electrical properties of the materials have not been studied. Knowledge of the electrical properties of the cubic MgZnO are required for its application in the fabrication of the micro-electronic devices, such as random access memory (RAM) and CMOS devices.

In this Letter, we report that cubic MgZnO thin film alloys have been deposited on Si substrates at low growth temperature. Morphological, structural and optical properties of the cubic MgZnO thin films are studied with respect to the guidelines for metal–insulator–silicon (MIS) device application. Then MIS have been fabricated using the cubic MgZnO thin films as insulators. Finally, the electrical characterizations including leakage current–voltage (I–V) and capacitance–voltage (C–V) for the MIS structures are performed.

Cubic MgZnO films were grown in a reactive e-beam evaporation system.[9] Ceramic $(MgO)_{0.1}(ZnO)_{0.9}$ target with high purity of 99.99% was used as the source material. The deposition of MgZnO thin films was carried out in oxidizing ambient

---

* Supported by the National Natural Science Foundation of China under Grant No 10174064, the Special Funding of Shanghai Nano-Promotion Centre (0352NM092) and Shanghai Applied Materials Foundation (No 0214).

** Email: hzwu@mail.sim.ac.cn

(high-purity oxygen gas introduced into the growth chamber) with chamber pressures of 2×10^{-4} Torr. The significant resistivity increases of MgZnO films grown under oxygen gas ambient indicate the effective ionization of a fraction of oxygen gas incorporated in the lattice. The ionization of oxygen gas in the growth chamber is attributed to the collision of oxygen gas with high-energy electron beams.

It is known that when oxide materials such as ZrO_2 and HfO_2 are grown on silicon, the elimination of an amorphous silicon oxide interfacial layer between high-*k* oxide dielectrics and Si substrate would be difficult because of oxygen diffusion into silicon substrates when growth temperature is high. This concern also exists in the growth of the cubic MgZnO thin films, though the low substrate temperature used in these growth experiments lessens the concern. To realize reliable growth experiments and the precise control of the SiO_2 interfacial layer, a thin SiO_2 layer (65 nm) on low-resistivity silicon substrates (0.01 Ωcm) had been intentionally formed by dry-oxygen oxidation method before the MgZnO film growth. This can prevent further oxidation of the silicon substrate during the MgZnO deposition that was performed under oxidizing ambient.

The cubic MgZnO thin films with various thickness (100–1500 nm) were deposited on SiO_2/Si(001) at the temperature of 250°C with the growth rate of $\sim 0.7\,\mu$m/h, which was calibrated by *ex situ* film thickness measurements using a TENCOR α-step profiler. Inductively coupled plasma (ICP) and optical absorption band edge measurements obtained the Mg composition in the ternary alloy as 55%.[10] A field emission scanning electron microscope (FE-SEM) and x-ray diffraction were used to analyse the interfacial structure and the crystallization of the oxide.

The deposited $Mg_{0.55}Zn_{0.45}O/SiO_2/Si$ (001) thin films were then subjected to the processing for the fabrication of MIS structures. The MIS structures were fabricated by photolithography and wet chemical etching. For the fabrication of $Al/Mg_{0.55}Zn_{0.45}O/SiO_2/Si$ MIS structures, the surfaces of the samples were ultrasonically degreased with organic solvents, rinsed in deionized water, and dried with nitrogen. The metallic contact for the epitaxial MgZnO surface of the structure was aluminium with thickness of 150 nm, which was deposited by electronic beam evaporation. The MIS structures were formed by photolithography with square Al patterns (area of 1.5×10^{-3} cm^2). They were then superficially etched in a concentrated solution of HPO_3 for 1 min at 60°C and in HF:H_2O (1:10) for 15 s. Finally the thinned Si substrate surface was also deposited with aluminium for Ohmic contact. The *I–V* characteristics were measured by an HP4156A semiconductor parameter analyser. High frequency (1 M Hz) *C–V* hysteresis curves were also acquired by sweeping the gate voltage from inversion to accumulation by an HP4280A impedance analyser with a slow varying voltage ramp rate (0.5 V/s) at room temperature.

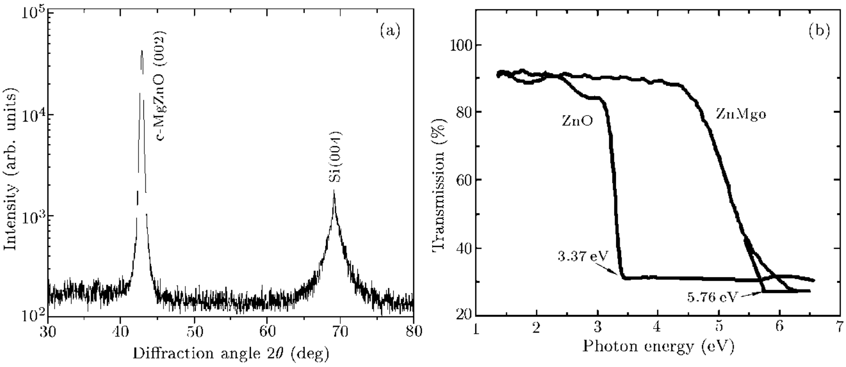

Fig. 1. (a) X-ray diffraction of cubic $Mg_{0.55}Zn_{0.45}O$ film grown on Si(001). (b) The comparison of transmission spectra for the cubic MgZnO and hexagonal ZnO films.

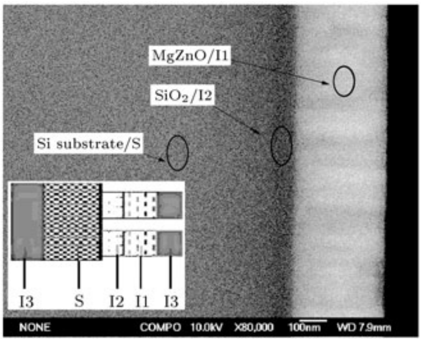

Fig. 2. A cross-sectional image of field-emission scanning electron microscope for the cubic $Mg_{0.55}Zn_{0.45}O$ film on Si with a 65 nm SiO_2 buffer. Inset: the fabricated MIS structure. I3, S, I2 and I1 denote Al electrodes, Si substrate, SiO_2 and MgZnO film, respectively.

The $Mg_{0.55}Zn_{0.45}O$ thin films grown on SiO_2/Si (001) are of cubic phase and crystalline with a preferential (001) orientation with the (002) diffraction peak dominating the XRD curve, as shown in Fig. 1(a). The dominant (002) diffraction peak from the cubic $Mg_{0.55}Zn_{0.45}O$ thin film is at 42.82° which is slightly smaller than the calculated diffraction angle (2θ) of 42.92° for cubic MgO ($a = 0.424$ nm). Figure 1(b) is the transmission spectra for the cubic $Mg_{0.55}Zn_{0.45}O$ and hexagonal ZnO epilayers grown on sapphire substrates using the same growth parameters as that of $Mg_{0.55}Zn_{0.45}O$ grown on Si. The fundamental absorption band edge for the cubic $Mg_{0.55}Zn_{0.45}O$ is higher than 5.5 eV, in comparison with 3.37 eV for the hexagonal ZnO films. The wider band gap of the cubic $Mg_{0.55}Zn_{0.45}O$ ($E_g > 5.5$ eV) is a fundamental criterion for the material to be used as high-κ dielectric which is a precondition to achieve low leakage current for MIS devices.[11] It can be seen in the transmission spectra that ZnO films demonstrate sharper absorption band edge than that for the cubic $Mg_{0.55}Zn_{0.45}O$ films. The declined absorption band edge for the $Mg_{0.55}Zn_{0.45}O$ films is attributed to the random distribution of Mg atoms in the ternary alloys, which is consistent with the broadened line width of the (002) XRD diffraction peak (FWHM=0.28.) for the cubic $Mg_{0.55}Zn_{0.45}O$ film shown in Fig. 1.

Figure 2 shows the cross-sectional FE-SEM micrograph for the cubic $Mg_{0.55}Zn_{0.45}O$ epitaxial layer on SiO_2/Si. A clear boundary is observed between the $Mg_{0.55}Zn_{0.45}O$ thin film and the SiO_2 layer which was formed on the Si substrate before the deposition of the $Mg_{0.55}Zn_{0.45}O$ thin film. In contrast, the interface between SiO_2 and Si is difficult to identify because of O^{2-} diffusion into the Si substrate in the process of the formation of SiO_2 layer by dry-oxygen oxidation. The thickness of the cubic $Mg_{0.55}Zn_{0.45}O$ film is 300 nm and the SiO_2 film is 65 nm as measured by the FE-SEM. The inset shown in Fig. 2 is the MIS device fabricated in this work. It is found that after HPO_3 etching, the surface of the MgZnO is shiny and smooth. No desquamation phenomenon was observed in the whole processing, which indicates good chemical bonding between the $Mg_{0.55}Zn_{0.45}O$ epilayer and the substrate.

Using the fabricated $Mg_{0.55}Zn_{0.45}O$ MIS device, electrical characterizations of the Al/$Mg_{0.55}Zn_{0.45}O$/SiO_2/n^+-Si pMOS capacitor was performed at room temperature. High frequency C–V hysteresis curves were acquired by sweeping the gate voltage from inversion to accumulation (forward sweep: −25 V to 20 V) and back to inversion (reverse sweep: 20 V to −25 V). A typical C–V characteristic curve for the MIS structure is shown in Fig. 3. The dielectric constant ε for the cubic $Mg_{0.55}Zn_{0.45}O$ is measured to be 10.7 (to be published).[12]

The equivalent oxide thickness (EOT) of high-κ dielectrics, $d_{\rm EOT}$, can be defined as

$$d_{\rm EOT} = \frac{\varepsilon_{rs}}{\varepsilon_{r0}} d_{\rm phy}, \tag{1}$$

where ε_{r0} is the dielectric constant of the high-κ material, ε_{rs} is the dielectric constant of silicon dioxide, and $d_{\rm phy}$ is the physical thickness of the ternary films. Interface characteristics of the MIS samples with different EOTs were studied by the conventional capacitance method,[13] via small ac signal admittance measurements at frequency 1 MHz. The charge polarity in the ternary films is determined from a flat band voltage shift $V_{\rm FB}$. The flat band capacitance $C_{\rm FB}$ can be obtained from the measured C–V curves and the following formula:

$$\frac{C_{\rm FB}}{C_0} = \frac{1}{1 + \frac{\varepsilon_{r0}}{\varepsilon_{r\rm Si}} \left(\frac{\varepsilon_{r\rm Si}\varepsilon_0 k_0 T}{q^2 N_d d_{\rm EOT}^2} \right)^{1/2}}, \tag{2}$$

where ε_{r0} and $\varepsilon_{r\rm Si}$ are the dielectric constants of oxide material and silicon (Si) respectively, k_0 is Boltzmann's constant, q is the electron charge, N_d is the donor doping density in the Si substrate, and C_0 and $d_{\rm EOF}$ are the capacitance and EOT of the insulating layer. From the calculated $C_{\rm FB}$ value and the C–V curve shown in Fig. 3, we know that the flat band voltage shift $V_{\rm FB}$ is 11.8 V. The positive flat band voltage shift for the $Mg_{0.55}Zn_{0.45}O$ layer indicates that the charges involved in the $Mg_{0.55}Zn_{0.45}O$ films are negative, which arise from the diffusion of the Si substrate of the high-density donor doping ($10^{19}/{\rm cm}^3$).

It can be seen from Fig. 3 that the hysteresis for the MIS structure is small ($\Delta V_{\rm FB} = 0.6\,{\rm V}$). The mobile charge density $D_{\rm mc}$ can be estimated from the measured $\Delta V_{\rm FB}$ by the following formula:

$$D_{\rm mc} = C_0 \frac{\Delta V_{\rm FB}}{A \cdot q}, \tag{3}$$

where A is the area of the capacitor and $\Delta V_{\rm FB}$ is the difference of flat band voltage shift between the forward and backward sweeping. The mobile charge density in the MIS device is calculated to be $5.57 \times 10^{10}\,{\rm cm}^{-2}$.

For comparison, MIS structures with SiO_2 layer on Si were also fabricated by the same procedure as the $Mg_{0.55}Zn_{0.45}O$ MIS device. The inset in Fig. 3 is the C–V result for the SiO_2/Si MIS structure. It is found that the $V_{\rm FB}$ value for the SiO_2/Si MIS structure is 3.4 V, which is smaller than that of the $Mg_{0.55}Zn_{0.45}O$ MIS structure. The mobile charge density $D_{\rm mc}$ from Eq. (3) is $1.9 \times 10^{11}{\rm cm}^{-2}$, which is larger than the $D_{\rm mc}$ value for the $Mg_{0.55}Zn_{0.45}O$ MIS structure. The lower mobile charge density for the $Mg_{0.55}Zn_{0.45}O$ MIS structure indicates that the $Mg_{0.55}Zn_{0.45}O$ films may not have high density of crystal boundaries and defects through which the mobile charge can tunnel.

The measured I–V characteristic for the MIS device of Al/300 nm $Mg_{0.55}Zn_{0.45}O$/65 nm SiO_2/n^+Si is shown Fig. 4(a). It can be seen that under the electrical field of 700 kV/cm, the leakage current density is very low, $5.0 \times 10^{-7}\,{\rm A/cm}^2$ for the device with 110 nm EOT and $5.4 \times 10^{-7}\,{\rm A/cm}^2$ for the device with 70 nm EOT. In contrast, as shown in Fig. 4(b), the leakage current density measured from the MIS structure that contains the 65 nm SiO_2 layer is rather higher, $\sim 10^{-3}\,{\rm A/cm}^2$.

The measured leakage current at room temperature consists of three different conduction mechanisms including Ohm current J_1, Fowler–Nordheim (F-N) tunnelling current J_2, and Frenkel–Poole (F-P) current J_3 which is generated from defects and electron traps in the insulators under high electrical field. The leakage current can be expressed in the form

$$J = a_1J_1 + a_2J_2 + a_3J_3, \qquad (4)$$

where $J_1 \sim E$, $J_2 \sim E^2\exp(-b_1/E)$, $J_3 \sim E\exp(b_2\sqrt{E})$, b_1 and b_2 are the constants, and E is the electrical field. The observed I–V characteristics in the $Mg_{0.55}Zn_{0.45}O$ MIS device (110 nm EOT) shown in Fig. 4 follow the Ohm current rule, while the I–V characteristics for the SiO_2 MIS device shown in the inset follow high electrical field F-P mechanism.[14,15]

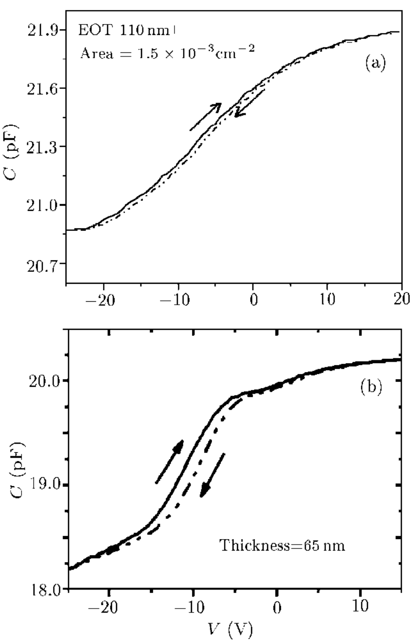

Fig. 3. (a) High-frequency (1 MHz) C–V characteristic for the $Mg_{0.55}Zn_{0.45}O$ MIS structure. (b) C–V characteristic for a SiO_2 MIS structure.

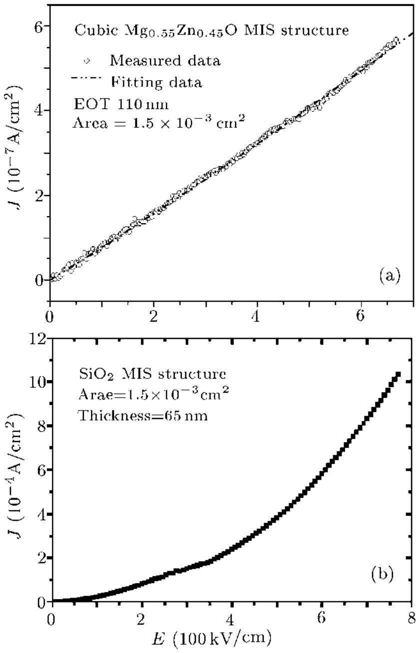

Fig. 4. (a) Leakage current density versus electrical field for the $Mg_{0.55}Zn_{0.45}O$ MIS structure. The dotted line is the measured data and the solid line is the fitting. (b) The leakage current density versus electrical field for the SiO_2 MIS structure.

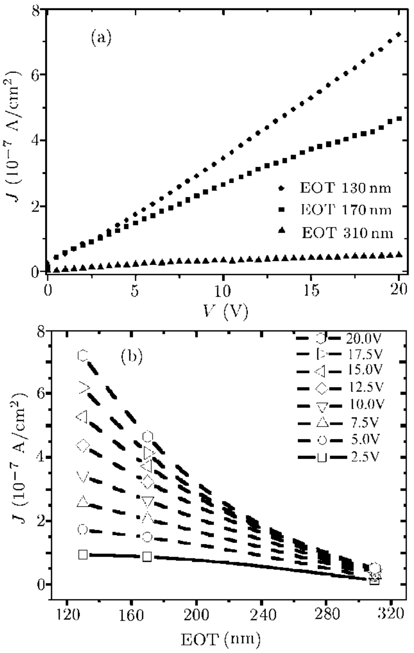

Fig. 5. (a) The leakage current density versus bias voltage for the cubic $Mg_{0.55}Zn_{0.45}O$ MIS structures with EOTs of 65, 110 and 250 nm. (b) The leakage current densities versus EOT at different bias-voltages.

Figure 5(a) shows the leakage current curves for three cubic $Mg_{0.55}Zn_{0.45}O$ MIS structures with EOT of 65, 110 and 250 nm. It can be seen that all three curves basically follow the Ohm current rule. As shown in Fig. 5(b), when the bias voltage is smaller than 10 V, for all three $Mg_{0.55}Zn_{0.45}O$ MIS devices, good linear dependence of leakage current densities on the EOTs is observed. However, when the bias voltage is higher than 15 V, which means a higher applied electrical field, the leakage current obviously deviates from the linear relation. The deviation from linear relation indicates that other conduction mechanisms, such as F-P mechanism and Schottky emission,[14–16] may be involved in the thin EOT (70 nm) sample.

In conclusion, we have successfully grown highly (001) oriented cubic $Mg_{0.55}Zn_{0.45}O$ on Si(001) by a reactive e-beam evaporation system. The cross section image of FE-SEM for the cubic $Mg_{0.55}Zn_{0.45}O$ film displays good morphology and high interfacial quality. The band gap of the cubic $Mg_{0.55}Zn_{0.45}O$ is measured to be higher than 5.5 eV. Using the cubic ternary thin films as an insulator, MIS structures have been fabricated. The C–V measurements show a flat band voltage shift V_{FB} of 11.8 V and mobile ion density D_{mc} of 5.57×10^{10} cm^{-2} for the MIS structure. Leakage current density as low as $\sim 10^{-7}$A/cm^2 is obtained at electrical field of 700 kV/cm. These unique structural and electrical properties of the fabricated MIS devices demonstrate that the cubic MgZnO grown on silicon is promising for the application to alternative gate dielectrics in silicon technology.

References

[1] Nishikawa Y et a 2002 *Appl. Phys. Lett.* **81** 4386
[2] Balog M et al 1972 *J. Cryst. Growth* **17** 298
[3] Lim S G et al 2002 *J. Appl. Phys.* **91** 4500
[4] Gurvitch M et al 1997 *Appl. Phys. Lett.* **51** 919
[5] Kwo J et al 2000 *Appl. Phys. Lett.* **77** 130
[6] Zhang N L et al 2003 *Chin. Phys. Lett.* **20** 273
[7] Choopun S et al 2002 *Appl. Phys. Lett.* **80** 1529
[8] Qiu D J et al 2003 *Chin. Phys. Lett.* **20** 582
[9] Wu H Z et al 2000 *J. Cryst. Growth* **217** 131
[10] Chen J et al 2003 *J. Phys.: Condens. Matter* **15** 475
[11] Wilk G D et al 2001 *J. Appl. Phys.* **89** 5243
[12] Wu H Z et al *Electron. Mater.* (accepted)
[13] Snow E H et al 1965 *J. Appl. Phys.* **36** 1664
[14] Frenkel J 1938 *Tech. Phys. USSR* **5** 685
[15] Frenkel J 1938 *Phys. Rev.* **54** 647
[16] Zhu W J et al 2002 *IEEE Electron. Dev. Lett.* **23** 97