行政院國家科學委員會專題研究計畫　成果報告

製備合成氧化物在互補式金氧半閘極介電層及自旋電元件應用之研究(III)

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計畫編號：NSC93-2215-E-009-037-
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計畫主持人：趙天生

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行政院國家科學委員會補助專題研究計畫成果報告

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計畫類別：■個別型計畫　　□整合型計畫

計畫編號：NSC93－2215－E－009－037－

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計畫主持人：趙天生　交通大學電子物理系 教授

共同主持人：Dr. Dolf Landheer (Principal Research Officer, Institute for Microstructural Sciences, National Research Council of Canada)

中　華　民　國　94 年 10 月 10 日

製備合成氧化物在互補式金氧半閘極介電層及自旋電元件應用之研究(III)

Deposition and Characterization of Compound Oxide Films for High-(CMOS Gate Dielectrics and Spintronics Applications (III)

計劃編號: NSC-93-2215-E-009-037
執行期間: 93/8/1~94/8/31

主持人：趙天生　交通大學電子物理系 教授
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ABSTRACT

(I) Low-temperature Hf Silicates:

Our work shows the deposition of high quality hafnium silicate ($HfSi_xO_y$) thin films with process temperatures below 250°C. Tetrakis(diethylamido) hafnium (TDEAH) and tris(*t*-pentoxy) silanol (TPOS) vapors were used as Hf and Si precursors, respectively. Alternative pulses of these two precursors allow a silicon-rich $HfSi_xO_y$ thin film to grow without additional oxidation steps. After a forming gas anneal, the Hf silicate films exhibited low leakage currents, relatively low interface-state densities (mid-gap D_{it} $\sim 3\times10^{11}$ $eV^{-1}cm^{-2}$), and negligible hysteresis (<20 mV). This would make them useful as gate dielectrics in thin-film transistors or as waveguiding and passivation layers in optoelectronic applications. After high-temperature annealing the electrical characteristics were further improved, showing that these films could also meet the requirements for a replacement gate-dielectric for SiO_2 in CMOS technology.

(II) Nickel Titanium Oxides:

$NiTiO_3$ high-*k* dielectrics were fabricated on N^+-doped poly-Si for the evaluations of interpoly-oxide and MIM applications. Thin Ni/Ti (5/5 nm) metal layers were sputter-deposited and then thermally oxidized into $NiTiO_3$ [2-3]. An NH_3 plasma treatment prior to the metal oxidation was found helpful to the oxide reliability. Samples with an NH_3 plasma pre-oxidation treatment exhibited better thermal stabilities over the control samples. Higher E_{bd} and Q_{bd} values were also demonstrated. TDDB and 10-year lifetime extractions showed that NH_3 plasma treated samples can sustain higher operation voltages. The enhanced reliability can be attributed to a smoother oxide surface observed in the AFM analysis. The effective dielectric *k* value was estimated to be 20~22. High-*k* $NiTiO_3$ dielectrics demonstrated potentials as alternative interpoly-oxides for FLASH memory devices. Floating-gate coupling ratio can be effectively increased by utilizing $NiTiO_3$ without a sophisticated gate stack design.

1. Introduction

In searching of alternative high-κ

materials for the gate-oxide, hafnium oxide (HfO_2) is a very promising choice. However, hafnium oxides crystallized at fairly low temperature (about 600^{o}C). When the crystallization happened, grain boundaries of hafnium oxides became leakage paths and degraded insulation properties. Therefore, hafnium silicate (HfSiO) has been looked into as a compromise between high k-value and good thermal stability.

Metal-organic chemical vapour deposition (MOCVD) technique is widely used in the semiconductor industry, and has been proved as a reliable method for thin-film epitaxy. However, for silicate deposition, the silicon precursor must be volatile and easy to decompose in processing temperature range. Recently it was shown that films with high silica contents can be deposited by atomic layer deposition (ALD) at low temperatures using metal alkylamides with tris(*t*-alkoxy) silanols [1]. Other low temperature processes for the deposition of silicon dioxide require the use of plasmas which can result in damage from ion-bombardment. Thus the ALD technique could be useful for many applications in electronic and optoelectronic devices. Our work shows the deposition of high quality hafnium silicate ($HfSi_xO_y$) thin films by ALD and MOCVD with process temperatures below 250°C.

In addition to hafnium silicates, we also evaluated the nitrogen incorporated $NiTiO_3$ dielectrics. The purpose of nitrogen incorporation is to suppress the crystallization, and to improve the electrical reliability. Since we haven't found suitable MOCVD precursors and process conditions for $NiTiO_3$, these $NiTiO_3$ films were fabricated by oxidation of sputtered thin metal films.

2. Experiments and Results

(I) Low-temperature Hf Silicates:

The MOCVD chamber is equipped with a liquid injection system (ATMI LDS-300B) for the hafnium precursor. A bubbler is installed to transport the silicon precursor into the chamber.

The TDEAH, a 0.1 M solution in octane, was used as the Hf precursor. The TDEAH was vaporized at 140 °C and then delivered into the chamber. Experimental substrates were HF-dipped Si <100> wafers, with the H termination replaced by 1-2 monolayers of SiO_2 formed by oxidizing the wafers in O_2 at 500 °C. The TPOS bubbler was held at 60 °C with 20 sccm nitrogen flowing through it. The pulse-mode deposition technique was used to produce hafnium silicate films. Depositions were done with a substrate temperature of 250 °C.

To see the carbon-contamination issue of deposited silicate films, a ~8 nm-thick film (in-situ Ellipsometry) was analyzed by XPS depth profiling. After a surface sputtering, the carbon signals became lower than the detection limits (Fig. 1), which suggested that most carbon contaminations were from the air exposure.

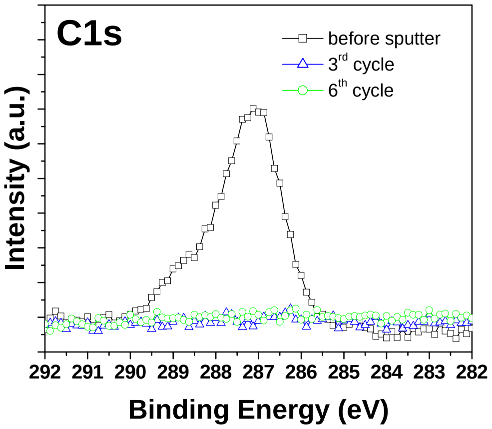

Fig.1 C1s XPS analysis of a Hf silicate film deposited with TDEAH and TPOS. Argon sputtering was used to remove the surface contamination and to see the depth profile

HRTEM analysis (Fig. 2) shows the amorphous structure of an as-deposited $Hf_{0.18}Si_{0.82}O_2$ film. The upper portion is darker, which implies a higher hafnium concentration in the upper layer. An energy dispersive X-ray spectrometer (EDS) line scan was performed along the film's cross-section. A slight increase of the silicon concentration was detected in the middle, corresponding to the bright layer in the TEM picture. The EDS line-scan also indicated that the aluminum gate may have reacted with the silicate films during the evaporation and created a top interfacial layer.

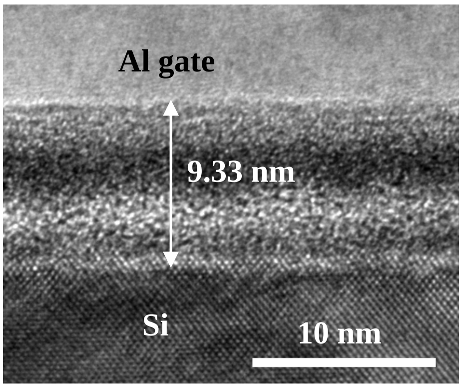

Fig. 2 HRTEM picture of an as-deposit film.

In Fig. 3(a), C-V curves of the as-deposit sample showed obvious frequency dispersion. There is also a hump in the C-V curve toward accumulation. It is believed that the appearance of the hump is due to P_b centers at the interface. A forming gas (4% H_2 + 96% N_2) anneal can alleviate the frequency dispersion and reduce the P_b centers. After a 450 °C forming gas anneal, the hysteresis in C-V curves can be effectively reduced. Fig. 3(b) shows I-V curves of the same $Hf_{0.18}Si_{0.82}O_2$ sample. The breakdown voltage was enhanced after a 380 °C forming gas anneal. When the annealing temperature was raised to 450 °C or higher, the soft breakdown phenomenon became more severe in the high electric-field region.

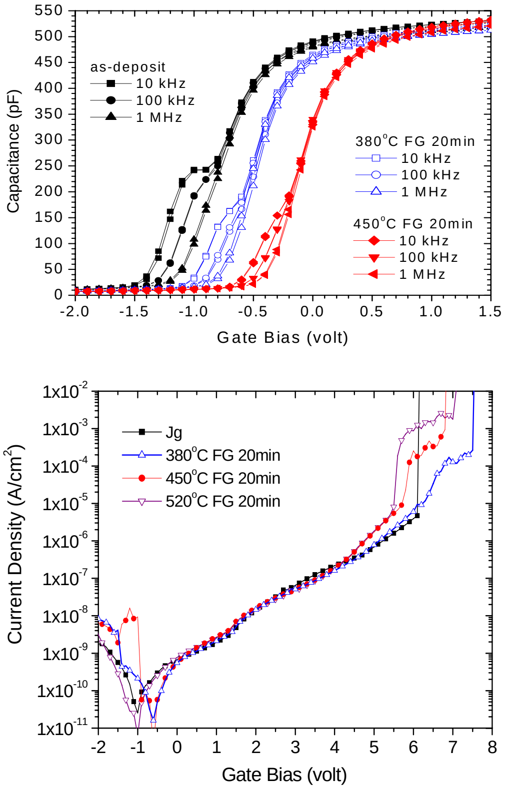

Fig. 3 (a) C-V and (b) I-V plots. Hf silicate films were treated with different RTA conditions.

(II) Nickel Titanium Oxides:

As shown in Fig. 4, samples with an NH_3 pre-oxidation plasma treatment showed improved stability even after a 900 °C post-oxidation RTA.

AFM analysis (Fig.5) showed the NH_3 pre-oxidation treatment can prevent the roughness-enhancement caused by thermal oxidation. The smoother oxide surface can also contribute to the improved electrical characteristics.

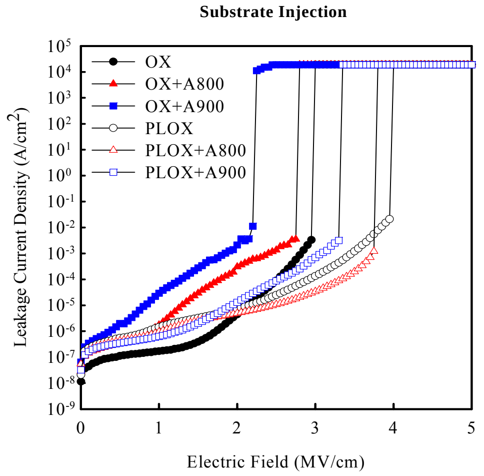

Fig.4 J-E characteristics of $NiTiO_3$ MIM capacitors. NH3 plasma treated samples (PLOX) showed better thermal stabilities after 800 °C or 900 °C anneals.

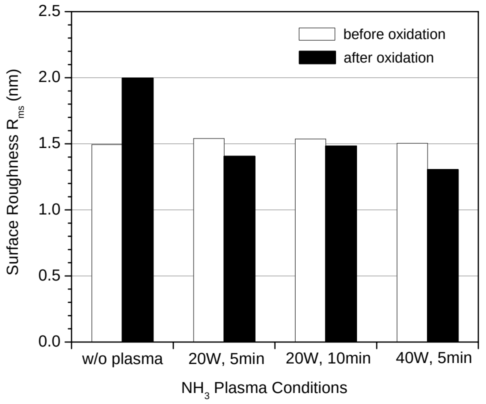

Fig. 5 The surface roughness analyzed by AFM. Ni/Ti metal thin films (before oxidation) and the oxidized $NiTiO_3$ are evaluated with different pre-oxidation plasma treatments.

3. Conclusions

(I) Low-temperature Hf Silicates:

Carbon-free hafnium silicate thin-films were deposited by using MOCVD with alternative pulses of TDEAH and TPOS precursors. Hafnium silicates with high silicon contents (Hf1-xSixOy, x>0.5) were deposited at 250 °C without additional oxidants or plasma-enhanced techniques. Chemical compositions (XPS date) of the $HfSi_xO_y$ remained stable when an 800 °C vacuum RTA was performed after the deposition. A forming gas anneal at a temperature ranging from 380 °C to 450 °C could further improve the hafnium silicate interface quality. This low-temperature process could be promising for TFT or optoelectronic applications.

(II) Nickel Titanium Oxides:

Interpoly NiTiO3 thin-films were fabricated by thermal oxidation of a Ni/Ti metal stack. When a pre-oxidation NH_3 plasma treatment was performed on the metal stack, the resulted NiTiO3 film showed better reliability: (1) improved thermal stability over leakage current behaviour, (2) higher breakdown field E_{bd}, (3) higher charge-to-breakdown value Q_{bd}, and (4) enhanced TDDB life-time. The best plasma condition is 20W 5min in this study. We believe the reliability improvements could be attributed to the Nitrogen incorporation and a smoother oxide surface.

4. References

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5. Publications

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[2] J.-H. Chen, D. Landheer, X. Wu, S. Moisa, G.I. Sproule, T.-F. Lei, T.-S. Chao, "$HfSi_xO_y$ Gate Dielectrics Prepared by Low-Temperature CVD Using Tetrakis(diethylamido) Hafnium with Tris(t-pentoxy) Silanol," presented at *the Twelfth Canadian Semiconductor Technology Conference*, Ottawa, August 16–19, 2004.

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