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High-k Materials

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The Structure of Plasma-Deposited and Annealed Pseudo-Binary ZrO_2-SiO_2 Alloys

G. Rayner Jr., R. Therrien, and G. Lucovsky

Departments of Physics, Electrical and Computer Engineering, and Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695-8202, USA

ABSTRACT

The internal structures of various $(ZrO_2)_x(SiO_2)_{1-x}$ alloys ($x \leq 0.5$) were investigated. A remote plasma enhanced-metal organic chemical vapor deposition (RPE-MOCVD) process was used to deposit films with varying alloy composition on Si(100) substrates. This study indicates that for the *glassy* silicate phase, g-$ZrSiO_4$, a glass transition temperature, T_g, exists between 800°C and 900°C at which phase separation into the end-member components, SiO_2 and ZrO_2, occurs.

INTRODUCTION

Pseudo-binary $(ZrO_2)_x(SiO_2)_{1-x}$ alloys are currently being considered as a high-k dielectric for microelectronic applications [1,2]. Due to post-deposition processing, one important issue is thermal stability of the internal structure. This paper identifies some limitations of these alloys for high-k dielectric applications. These limitations are associated with the thermal stability of the stoichiometric silicate phase, $ZrSiO_4$.

EXPERIMENTAL

Films were deposited by a RPE-MOCVD process described elsewhere [1] onto Si(100) substrates. Film composition was determined by Rutherford backscattering spectrometry (RBS). Alloy internal structure, as-deposited and following subsequent annealing, was characterized by X-ray diffraction (XRD) and infrared (IR) absorption spectroscopy. Post deposition 60s anneals at 600°C, 700°C, 800°C, and 900°C were performed *ex-situ* on each sample in an inert argon ambient using an AG Minipulse 310 RTA unit. XRD measurements were made using a Bruker x-ray diffractometer with a beryllium area detector centered at the following 2θ positions: 25° and 50°. IR absorption measurements in the mid-IR regime (4000-$400 cm^{-1}$) were carried out on a Nicolet Magna-FTIR 750 spectrometer. Due to the relatively slow deposition rate (~ 4 Å/min), films were deposited for eight hours to ensure that the thickness was sufficient for good IR absorption sensitivity.

RESULTS AND DISCUSSION

A portion of the equilibrium compositional phase diagram [3] for the pseudo-binary ZrO_2-SiO_2 system is presented in Fig. 1. This figure illustrates only the chemical phase of each component and not any particular structural phase. The phase diagram, for temperatures below ~1600°C, can be divided into two regions based on chemical composition: 1) a SiO_2-rich region ($0 \leq x < 0.5$) from SiO_2 to the silicate phase, $ZrSiO_4$, and 2) a ZrO_2-rich region ($0.5 < x \leq 1$) from the silicate phase to the end-member, ZrO_2. Above ~1600°C, $ZrSiO_4$ phase separates into the end-member components, SiO_2 and ZrO_2 ($ZrSiO_4 \rightarrow ZrO_2 + SiO_2$). It must be emphasized that this transition temperature corresponds to the crystalline silicate phase, c-$ZrSiO_4$. Included in this diagram is the glass transition temperature, T_g, which corresponds to the temperature at which the *glassy* silicate phase, g-$ZrSiO_4$, softens. This aspect of the phase diagram will be discussed later.

Rutherford Backscattering Spectrometry

Film composition as a function of depth was determined by Rutherford backscattering spectrometry. This study investigated three ZrO_2-SiO_2 alloys. RBS results indicate that, within experimental uncertainty, both species are fully oxidized (i.e., %O = 66.7%, %Si + %Zr = 33.3%) having only Si-O and Zr-O bonds. RBS depth profiling reveals that ZrO_2-composition varies as a function of depth in each film. The data shows that ZrO_2-compositon increases as a function of film depth having the highest composition near the Si-interface. With increasing ZrO_2 incorporation variations in composition as a function of depth become more significant. For each $(ZrO_2)_x(SiO_2)_{1-x}$ alloy, Table I lists the average value of x and the overall change in x, Δx. The overall change in composition, Δx, is the measured value of x near the Si-interface minus the value near the film surface. Also included in Table 1 is the compositional uncertainty for each species. According to RBS, films are approximately 2000 Å thick.

X-Ray Diffraction

The XRD results of Zr10 are presented in Fig. 2a. As-deposited, a weak, broad feature is observed at a 2θ value of approximately 23° indicating the film is amorphous. No changes in structure are observed after annealing. Similarly, XRD results of the alloy with intermediate ZrO_2-composition, Zr20, in Fig. 2b indicate a stable amorphous structure. The XRD data of as-deposited Zr50 in Fig. 2c has a relatively strong, broad feature at approximately 30° indicative of an amorphous phase. No changes in structure are observed when annealed up to 800°C; however, crystallization occurred at 900°C, and the structural phase was identified as tetragonal-ZrO_2.

Infrared Absorption Spectroscopy

The IR absorption spectra of the two end-members in Fig. 1, SiO_2 and ZrO_2, can be used to establish a basis for understanding the IR response of the ZrO_2-SiO_2 alloy system. IR spectra of the two end-members, both as-deposited and following a 900°C anneal, are presented in Fig. 3. The local bonding in SiO_2 is made up entirely of covalent Si-O-Si bonds. In general, covalent-oxide glasses form continuous random network (CRN) structures that are stable when heated to relatively high temperatures. The IR spectra of the a-SiO_2 film in Fig. 3 has three characteristic features: i) a stretching-mode vibration at ~ 1070 cm^{-1}, ii) a bending-mode vibration at ~ 810 cm^{-1}, and iii) a out-ofplane rocking-mode vibration at ~ 455 cm^{-1}. Each Si-atom in the network has four equivalent oxygen nearest neighbors which results in the high wavenumber shoulder at ~ 1200 cm^{-1}. After annealing at 900°C there is no significant change in the IR response indicating the internal structure is thermodynamically stable.

Local bonding in ZrO_2 is characterized by ionic Zr-O-Zr bonds. In contrast to covalent-oxide glasses, ionic-oxide glasses form random close packed (RCP) structures which are not thermodynamically stable (i.e., they readily crystallizes when relatively small amounts of energy in the form of heat is added). The as-deposited film in Fig. 3 has spectral features associated with a polycrystalline monoclinic phase of ZrO_2, as determined by XRD. Note that these features, which are due to stretching-mode vibrations of ionic Zr-O bonds, are observed in the region from ~ 400-800 cm^{-1}. The IR response remains unchanged following a 900°C anneal indicating no changes in internal structure.

The IR absorption spectra of Zr10 in Fig. 4a has features at ~ 1067 cm^{-1}, ~ 810 cm^{-1}, and ~ 450 cm^{-1} that are indicative of an a-SiO_2 covalent CRN structure previously discussed. The incorporation of ZrO_2 into the a-SiO_2 matrix results in the formation of Si-O-Zr bonds. Since the bonding between zirconium and oxygen, according to Pauling electronegativity, is mainly ionic, the Zr-atoms act as a network modifier and not as part of the network structure. Therefore, the shoulder observed at ~ 950 cm^{-1} is assigned to a stretching-mode vibration of the non-bridging oxygen atoms, Si-O^{-1}, associated with Si-O-Zr bonds. The IR response after successive anneals indicates that the internal structure is relatively stable.

IR results of Zr20 in Fig. 4b are similar to those obtained for Zr10. However, as a result of increased ZrO_2 composition, changes in the internal structure related to ZrO_2 incorporation into the a-SiO_2 matrix now becomes more apparent. Specifically, a broadening of the shoulder at ~ 950 cm^{-1} and a broad band of modes extending from ~ 400-800 cm^{-1} are observed due to the increase of Si-O-Zr bonding. From the previous discussion on the IR response of c-ZrO_2 in Fig. 3, the band of modes from ~ 400-800 cm^{-1} are due to stretching-mode vibrations related to Zr-O bonds. The internal structure is relatively stable up to 800°C, but at 900°C modes assigned to Zr-O bonds show some evidence of structural change indicated by a weak shoulder at ~ 600 cm^{-1} in the IR response.

The IR absorption spectra of the alloy having the highest ZrO_2-composition, Zr50, is shown in figure 4c. For annealing temperatures up to 800°C no evidence of a bending-mode vibration at ~ 810cm^{-1} is observed indicating the absence of an a-SiO_2 CRN structure. Since no Zr-O stretching-modes are observed above ~ 800 cm^{-1} in Fig. 3, features from approximately 800-1200 cm^{-1} must be due to vibrational modes related to tetrahedral SiO_4^{-4} molecular-ions. Features from approximately 400-800 cm^{-1} contain a superposition of modes related to SiO_4^{-4} molecular-ions, and ionic Zr-O bonds. Therefore, the internal structure of the as-dep. film is mostly the *glassy* stoichiometric phase, g-$ZrSiO_4$, where each O-atom forms only Si-O-Zr bonds. After annealing up to 800°C, the internal structure is relatively stable. However, at 900°C the internal structure changes rather dramatically. The presence of a bending mode vibration at ~ 810 cm^{-1} indicates that an a-SiO_2 network is now present. Also, the large decrease in the intensity of modes ranging from ~ 800-1000 cm^{-1} indicates that a large number of Si-O-Si and Zr-O-Zr bonds were formed (i.e., $2\cdot\text{Si-O-Zr} \rightarrow \text{Si-O-Si} + \text{Zr-O-Zr}$). Using XRD results in Fig. 3c, the features at ~ 450 cm^{-1}, and ~ 600 cm^{-1} are now dominated by tetragonal phase c-ZrO_2. The reduced number of sharp features, relative to c-ZrO_2 monoclinic-phase in Fig. 4, is consistent with the increased symmetry of the tetragonal-phase.

The transition from Si-O-Zr bonding to Si-O-Si and Zr-O-Zr bonding at 900°C in Zr50 indicates chemical separation of the g-$ZrSiO_4$ phase. The shoulder at 600cm^{-1} in Fig. 4c related to the chemical phase, ZrO_2, is also weakly observed in Zr20 following a 900°C anneal indicating that regions containing only Zr-O-Zr bonds are present in this alloy as well. Results indicate that the glass transition temperature, T_g, for the g-$ZrSiO_4$ phase is somewhere between 800°C and 900°C. At temperature, T_g, Si-O bonds begin to break allowing the g-$ZrSiO_4$ phase to separate into the end-member components, SiO_2 and ZrO_2. In the crystalline phase, this separation does not occur until ~1600°C.

CONCLUSIONS

The experimental results indicate that the as-deposited films are chemically ordered having only Si-O-Si and Si-O-Zr bonds consistent with the equilibrium phase diagram. Both IR and XRD indicate that the internal structure is relatively stable up to 800°C. However, at 900°C results indicate that g-$ZrSiO_4$ chemically phase separates forming regions containing only Si-O-Si and Zr-O-Zr bonds, with Si-O-Zr bonds occurring only at internal boundaries. These results indicate limitations of these alloys for high-k dielectric applications due to: 1.) chemical phase separation resulting in lower effective dielectric constants, and 2.) crystallization of regions containing ZrO_2 which can lead to high leakage currents. Further investigation is needed to determine how these results are related to film thickness.

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Table I. RBS results indicate that ZrO_2-composition increases as a function of depth; therefore, only the average value of x is reported here. The overall change in composition, Δx, is the measured value of x near the Si-interface minus the value near the film surface.

Fig. 1 A portion of the equilibrium compositional phase diagram for the $(ZrO_2)_x(SiO_2)_{1-x}$ alloy system. The black dots represent the samples discussed in this paper.

Fig. 2a The XRD results of Zr10 as-deposited and after annealing. The weak, broad feature at ~ 23° indicates an amorphous structure.

Fig. 2b The XRD results of Zr20 as-deposited and after annealing.

Fig. 2c The XRD results of Zr50 as-deposited and after annealing. The relatively strong, broad feature at ~ 30° indicates an amorphous structure. However, at 900°C crystallization occurred and the structural phase was identified as tetragonal ZrO_2.

Fig. 3 IR absorption spectra of the two end-members components, SiO_2 and ZrO_2, as-deposited and after a 900°C anneal.

Fig. 4a IR absorption spectra of Zr10 as-deposited and after annealing. The shoulder observed at ~ 950 cm^{-1} is assigned to a stretching-mode vibration of the non-bridging oxygen atoms, $Si\text{-}O^{-1}$, associated with Si-O-Zr bonds.

Fig. 4b IR absorption spectra of Zr20 as-deposited and after annealing. At 900°C modes assigned to Zr-O bonds show evidence of structural change indicated by a weak shoulder at ~ 600 cm^{-1}.

Fig. 4c IR absorption spectra of Zr50 as-deposited and after annealing. At 900°C the presence of a bending mode vibration at ~ 810 cm^{-1} indicates an a-SiO_2 CRN structure.

RBS Results

Sample	x (Avg. ±1.5%)	Δx
Zr10	0.10	0.033
Zr20	0.229	0.069
Zr50	0.50	0.102

* Experimental Uncertainty: %O ±6%, %Si ±2%, %Zr ±0.5%

Table I

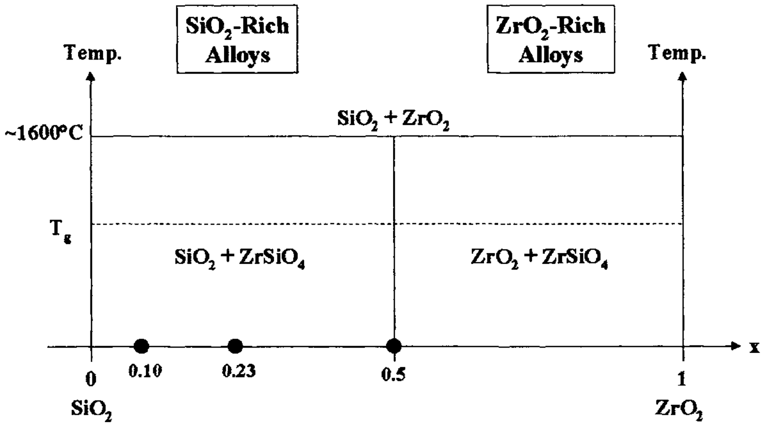

Fig. 1

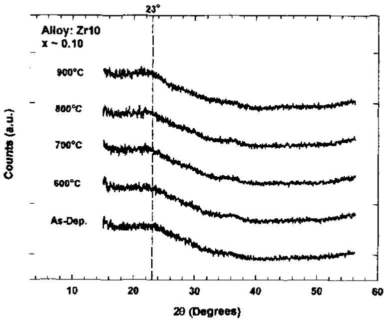

Fig. 2a

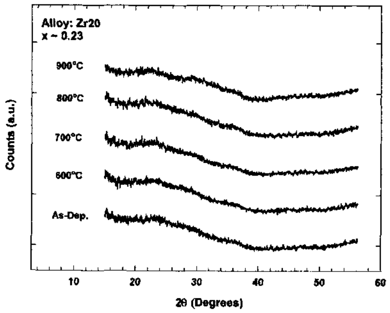

Fig. 2b

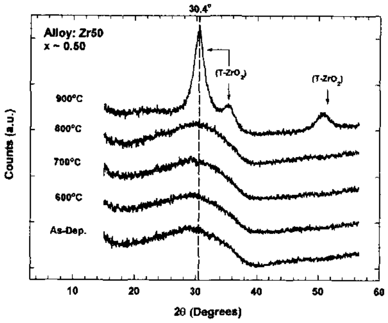

Fig. 2c