Miscibility of amorphous $\text{ZrO}_2\text{--Al}_2\text{O}_3$ binary alloy

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(Received 4 September 2001; accepted for publication 15 January 2002)

Miscibility is a key factor for maintaining the homogeneity of the amorphous structure in a $\text{ZrO}_2\text{--Al}_2\text{O}_3$ binary alloy high- k dielectric layer. In the present work, a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ laminate thin layer has been prepared by atomic layer chemical vapor deposition on a Si (100) wafer. This layer, with artificially induced inhomogeneity (lamination), enables one to study the change in homogeneity of the amorphous phase in the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ system during annealing. High temperature grazing incidence x-ray diffraction (HT-XRD) was used to investigate the change in intensity of the constructive interference peak of the x-ray beams which are reflected from the interfaces of $\text{ZrO}_2/\text{Al}_2\text{O}_3$ laminae. The HT-XRD spectra show that the intensity of the peak decreases with an increase in the anneal temperature, and at 800 °C, the peak disappears. The same samples were annealed by a rapid thermal process (RTP) at temperatures between 700 and 1000 °C for 60 s. Room temperature XRD of the RTP annealed samples shows a similar decrease in peak intensity. Transmission electronic microscope images confirm that the laminate structure is destroyed by RTP anneals and, just below the crystallization onset temperature, a homogeneous amorphous ZrAl_xO_y phase forms. The results demonstrate that the two artificially separated phases, ZrO_2 and Al_2O_3 laminae, tend to mix into a homogeneous amorphous phase before crystallization. This observation indicates that the thermal stability of $\text{ZrO}_2\text{--Al}_2\text{O}_3$ amorphous phase is suitable for high- k applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1459765]

ZrO_2 -based oxide layers, ZrO_2 ,^{1–5} Zr silicates,^{6,7} and Zr aluminates⁸ have attracted the attention of researchers who are looking for high- k dielectric materials to replace SiO_2 in complementary metal–oxide–semiconductor (CMOS) transistors. The requirements for high- k materials can be summarized as the following: (1) a high k value (dielectric constant), (2) chemical stability at high temperatures, (3) large band gap, and (4) structural homogeneity. Pure ZrO_2 meets all requirements except that of structural homogeneity. Since amorphous ZrO_2 crystallizes at around 500 °C, the ZrO_2 layers will be crystalline after a postthermal cycle in conventional CMOS process flow. Crystallization induces problems such as grain boundary leakage and nonuniformity in the k value and the film thickness.^{2,9} Zr silicates with certain compositions have a crystallization onset temperature as high as 900 °C, which is near the postannealing temperature used in conventional processing flow. However, phase separation has been found in amorphous Zr-rich silicates at temperatures below the onset of crystallization,^{6,7} which also results in structural inhomogeneity. Phase separation, or immiscibility, is a phenomenon that is known to exist in amorphous binary systems.¹⁰ In some systems including the $\text{ZrO}_2\text{--SiO}_2$ system, immiscibility exists even in the stable liquid phase

(above the melting point). Figure 1(a) shows a phase diagram of the $\text{ZrO}_2\text{--SiO}_2$ system, in which a stable immiscibility zone exists between 60–80 mol % SiO_2 . This stable immiscibility zone can be extended to temperatures lower than the melting point, and gives a metastable immiscibility zone in a wide composition range, where phase separation occurs in an amorphous state. In previous work,⁸ we proposed Zr aluminate as a possible high- k dielectric material based on an analysis of the k value, band gap, and chemical stability expected. The phase diagram of the $\text{ZrO}_2\text{--Al}_2\text{O}_3$ system shown in Fig. 1(b) reveals that the thermostability of this system might meet the requirement for high- k materials. In a wide composition range (30–80 mol % Al_2O_3), the system has a relatively low melting point. Thus a high crystallization onset temperature is expected in this composition range. It is also important that there is no stable immiscibility zone in this system. Experimental work⁸ has shown that $\text{ZrO}_2\text{--Al}_2\text{O}_3$ binary alloys with 42 and 61 mol % Al_2O_3 remain amorphous and homogeneous after a rapid thermal process (RTP) anneal at 900 °C for 1 min. No phase separation has been found in these homogeneous binary alloys before crystallization.

In this letter, the miscibility of the $\text{ZrO}_2\text{--Al}_2\text{O}_3$ binary system is studied in more detail. The idea is to induce inhomogeneity artificially by deposition of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ laminate structure, and then to observe the change in structure

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FIG. 1. (a) Phase diagram of the ZrO_2 - SiO_2 system, showing stable and metastable immiscibility (redrawn according to Ref. 11). (b) Phase diagram of the ZrO_2 - Al_2O_3 system (redrawn according to Ref. 12).

during thermal annealing. If the separated ZrO_2 and Al_2O_3 phases tend to mix during annealing before crystallization, we reach the conclusion that the amorphous mixture of the ZrO_2 - Al_2O_3 binary system remains homogeneous during annealing below the crystallization onset temperature.

A layer with a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ laminate structure was deposited on a Si (100) wafer by workers at ASM Microchemistry into an F-450 atomic layer chemical vapor deposition (ALCVD) reactor. TMA [$\text{Al}(\text{CH}_3)_3$] and water were used as precursors for the deposition of Al_2O_3 , and ZrCl_4 and water was used for ZrO_2 . The deposition starts with 15 cycles of Al_2O_3 deposition. Then eight cycles of ZrO_2 deposition were conducted, forming the first lamina, followed by five cycles of Al_2O_3 deposition for the second lamina. Such a double laminae (8 cycle ZrO_2 +5 cycle Al_2O_3) deposition was repeated 98 times. The final step was again 15 cycles of Al_2O_3 deposition. Thus a multilayer structure of 15 cycles Al_2O_3

FIG. 2. HT-XRD spectra of the sample collected at different temperatures.

FIG. 3. XRD spectra of the samples after RTP anneals at different temperatures.

+ (8 cycles ZrO_2 +5 cycles Al_2O_3) $\times$ 98+15 cycles Al_2O_3 was prepared.

High temperature grazing incidence x-ray diffraction (HT-XRD) was conducted on the above sample using the Seifert 3003 TT x-ray diffractometer system. The setup and experimental conditions of the HT-XRD are described elsewhere.^{13,14} RTP annealing (rapid heating, 1 min holding, in a N_2/H_2 atmosphere) was done at different temperatures. X-ray diffraction spectra of the annealed samples were collected with the same diffractometer at room temperature. High resolution transmission electron microscopy (HRTEM) was used to study the homogeneity of the amorphous phase and the morphology of the annealed samples. The composition of the sample was determined by x-ray fluorescence (XRF) (Philips Technos PW-2400 XRF).

Figure 2 shows a room temperature XRD spectrum of the as-deposited sample and the HT-XRD spectra collected at different temperatures. In the spectrum of the as-deposited sample, a broad band is found between 20° and 40° , with a maximum around 30° . This type of broad band is characteristic of amorphous phase and is attributed to the scattering of x rays by the short-range order in the amorphous phase. Besides the broad band, a sharp, intense peak appears at $2\theta = 11.6^\circ$. Given the use of $\text{Cu } K\alpha$ radiation, this angle corresponds to diffraction spacing of about 0.76 nm. This peak can be attributed to constructive interference of x rays reflected from the interfaces between the two separated phases. TEM observation shows that the thickness of the whole deposit is about 77 nm. The thickness of every $\text{ZrO}_2/\text{Al}_2\text{O}_3$ double laminae, i.e., the spacing of the correlative interfaces, is around 0.77 Å, in good agreement with the diffraction spacing obtained from the XRD spectrum.

In comparing the HT-XRD spectra measured at different temperatures, one finds that the intensity of the peak around $2\theta = 11.6^\circ$ decreases with an increase in temperature. Below 600°C , the decrease is small. Above 600°C , it decreases fast, and approaches zero at 800°C . The broad band between 20° and 40° does not change much below 700°C , indicating that the deposit remains amorphous. At 800°C , a very small peak appears at 30° , corresponding to the onset of crystallization. From the position of the peak and the fact that tetrag-

FIG. 4. Cross-sectional TEM images of the as-deposited and the RTP annealed samples.

onal ZrO_2 is much more stable than cubic ZrO_2 at room temperature, we can conclude that the predominant crystalline phase is tetragonal ZrO_2 . Similar results have been found in the XRD spectra of RTP annealed samples, shown in Fig. 3. In the spectrum of the sample annealed at 700 °C, the broad band between 20° and 40° and the intense, sharp peak at $2\theta=11.6^\circ$ can be seen. After RTP at 800 °C, the broad band shows no change. The intensity of the sharp peak, however, decreases to a large extent. After the RTP at 900 °C, the sharp peak has disappeared. At the same time, a diffraction peak appears at $2\theta\sim 30^\circ$, indicating the formation of tetragonal ZrO_2 . The intensity of this peak increases further when the temperature is increased to 1000 °C, implying an increase of the volume fraction of the crystalline phase in the layer. The above results demonstrate that a process of mixing occurs during annealing. Below 600 °C, the laminate structure does not change much. Above 600 °C, the laminate structure is damaged by interdiffusion of the atoms across the interfaces. This reduces the x-ray reflectivity of the interfaces. At 800 °C, a homogeneous mixture forms.

TEM observation of the annealed samples confirmed the above results. Figure 4 shows TEM images of the as-deposited and annealed samples. In the as-deposited sample, the laminate structure is distinguishable as separate layers with different contrasts. This laminate structure is homogenized after the RTP anneal at 700 °C, and disappears when the RTP anneal temperature increases to 800 °C. After the annealing at 900 °C, tetragonal ZrO_2 crystallites appear in the amorphous matrix.

The above results show clearly that the two separated phases, ZrO_2 and Al_2O_3 , tend to mix into a homogeneous mixture before crystallization. This implies that the homogeneous amorphous mixture, ZrAl_xO_y , is thermodynamically

more stable than the separated two phases. At temperatures below 600 °C, the tendency toward mixing already exists. The high viscosity inhibits the moving of atoms across the interface of the neighboring laminae. Heating reduces the viscosity, or increases the mobility of the atoms, and thus enables the system to evolve to its more stable state. Below the crystallization onset temperature, the homogeneous amorphous mixture is stable. Above the crystallization onset temperature, the crystalline phase is stable. These conclusions agree with the observations of homogeneous Zr_2AlO_y during annealing,⁸ where no amorphous phase separation has been observed before crystallization.

Compared to the homogeneous Zr_2AlO_y film (M2 in Ref. 8), the layer with the laminate structure presented here shows a lower crystallization onset temperature. This lower crystallization onset temperature can be attributed to the difference in composition in the two cases. The layer with the laminate structure studied in this letter has about 26 mol % Al_2O_3 , while the homogeneous layer (M2 in Ref. 8) has 42 mol % Al_2O_3 . Since ZrO_2 has a much lower crystallization onset temperature than Al_2O_3 , doping of Al_2O_3 in ZrO_2 raises the crystallization onset temperature. The extent of the increase is expected to depend on the concentration of Al_2O_3 . The more Al_2O_3 , the higher the crystallization onset temperature of the mixture. Further study of the composition dependence of the crystallization onset temperature and of other properties such as the band gap and k values is being conducted and the results will be reported.

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