

# IBM Research Report

## Materials Characterization of $\text{ZrO}_2\text{-SiO}_2$ and $\text{HfO}_2\text{-SiO}_2$ Binary Oxides Deposited by Chemical Solution Deposition

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## Materials characterization of $\text{ZrO}_2\text{-SiO}_2$ and $\text{HfO}_2\text{-SiO}_2$ binary oxides deposited by chemical solution deposition

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### ABSTRACT

The thermal stability, microstructure, and electrical properties of  $x\text{ZrO}_2(100-x)\text{SiO}_2$  (ZSO) and  $x\text{HfO}_2(100-x)\text{SiO}_2$  (HSO) ( $x= 15, 25, 50, 75\%$ ) binary oxides were evaluated to help assess their suitability as a replacement for silicon dioxide gate dielectric in complementary metal oxide semiconductor (CMOS) transistors. The films were prepared by chemical solution deposition (CSD) using a solution prepared from a mixture of zirconium, hafnium and silicon butoxyethoxides dissolved in butoxyethanol. The films were spun onto  $\text{SiO}_x\text{N}_y$  coated Si wafers and furnace annealed at temperatures from 500-1200 °C in oxygen for 30 minutes. The microstructure and electrical properties of ZSO and HSO films were examined as a function of Zr/Si and Hf/Si ratio and annealing temperature. The films were characterized by X-ray diffraction, FTIR, RBS and AES. At  $\text{ZrO}_2$  or  $\text{HfO}_2$  concentrations  $\geq 50\%$ , phase separation and crystallization of tetragonal  $\text{ZrO}_2$  and  $\text{HfO}_2$  was observed at 800 °C. At  $\text{ZrO}_2$  or  $\text{HfO}_2$  concentrations  $\leq 25\%$ , phase separation and crystallization was observed at 1000 °C. As annealing temperature increased, a progressive change in microstructure was observed in the FTIR spectra. Additionally, the FTIR spectra suggest that  $\text{HfO}_2$  is far more disruptive of the silica network than  $\text{ZrO}_2$  even at  $\text{HfO}_2$  concentrations  $\leq 25\%$ . The dielectric constant of the 25, 50 and 75% ZSO films were measured and were observed to be less than the linear combination of  $\text{ZrO}_2$  and  $\text{SiO}_2$  dielectric constants. The dielectric constant was observed to increase with increasing  $\text{ZrO}_2$  content. The dielectric constant was also observed to be annealing temperature dependent with larger dielectric constants observed in non-phase separated films. The Clausius-Mossotti equation and a simple capacitor model for a phase separated system was observed to fit the data with the prediction that to achieve a dielectric constant larger than 10 doping concentrations of  $\text{ZrO}_2$  would have to be greater than 70%.

## INTRODUCTION

ZSO and HSO are possible replacements for silicon dioxide as the gate dielectric material for standard complementary metal oxide semiconductor (CMOS) transistors.<sup>1-3</sup> ZSO and HSO materials are reported to be thermodynamically stable in contact with silicon. However, little understanding has been gained as to how ZSO and HSO films will behave with full processing treatments utilizing implant activation anneals at temperatures up to 1000 °C. Many of the bulk properties of ZSO and HSO are dependent on the exact preparation conditions and are related to the connectivity and type of ZrO<sub>x</sub> and SiO<sub>x</sub> polyhedra present in the structure. We have utilized chemical solution deposition (CSD) as a quick and inexpensive means of bulk materials screening. Unlike chemical vapor deposition or physical vapor deposition, CSD requires no vacuum equipment, no deposition tool development, and no process development time to obtain desired stoichiometries (solution concentration is film concentration). By utilizing a stable solution chemistry with no aging effects, solutions can be prepared and stored indefinitely between spinnings and still obtain the same quality film.<sup>4-5</sup> Bulk xerogels and glasses of ZSO have been prepared by CSD with different solution chemistries,<sup>7-16</sup> however no report exists describing the deposition of HSO or ZSO by CSD utilizing a butoxyethanol based chemistry. In an attempt to gain a better understanding of the materials properties of ZSO and HSO we have prepared films of ZSO and HSO and characterized their microstructural and electrical properties.

## EXPERIMENTAL

### Chemical Solution Deposition of ZSO and HSO

ZSO and HSO films of various compositions in the  $x\text{ZrO}_2\cdot(100-x)\text{SiO}_2$  (ZSO) and  $x\text{HfO}_2\cdot(100-x)\text{SiO}_2$  (HSO) ( $x= 15, 25, 50, 75\%$ ) systems were fabricated by CSD. The CSD solutions were prepared from a mixture of zirconium, hafnium and silicon butoxyethoxides dissolved in butoxyethanol.<sup>4-5</sup> The films were deposited by spin casting on (5-20 Å) SiO<sub>x</sub>N<sub>y</sub> coated Si substrates. The Zr/Si and Hf/Si ratio was varied by mixing a Zr or Hf butoxyethoxide solution and a separate Si butoxyethoxide solution and spinning the mixed solution. After loading the spinning solution into a syringe and attaching 0.45 and 0.1 μm syringe filters, the mixed spinning solution was syringed on the substrate until completely wetted. The substrate was then spun for 20 sec at 2000-4000 rpm onto a Si substrate which had been preheated on a 350 °C hot plate. After each spin-coating, the samples were baked on a hot plate at 150 °C for 1-3 min, then at 350 °C for 3-10 minutes in air. ZSO and HSO film thickness was varied by solution concentration, by spinning speed, and by depositing multiple layers with a hot plate bake anneal between each layer. The final film was hot plate baked at 350 °C for a minimum of 30 minutes before furnace annealing at 500, 700, 800, 900, 1000, or 1100 °C for 30 min or 1200 °C for 60 min in flowing oxygen. Film thickness was controlled at 1000 Å for electrical measurements and 2000-3000 Å for XRD and FTIR analysis.

## **ZSO Film Characterization**

X-ray diffraction (XRD) spectra were obtained using a Philips PW1729 diffractometer with Cu K $\alpha$  radiation. The FTIR spectra were recorded with a Nicolet PCIR 5 spectrometer using an uncoated wafer as the background. For FTIR and X-ray diffraction (XRD) analysis, film thickness were at least 2000 Å thick. Rutherford backscattering (RBS) and Auger electron spectroscopy (AES) was conducted on two 75% ZSO films, 1000 Å thick, deposited on a 10 Å SiO<sub>x</sub>N<sub>y</sub> interface and annealed at 900 and 1100 °C for 30 minutes in flowing oxygen. The AES spectral data for the two profiles were analyzed together to insure that the peaks were measured exactly the same way. Overlapping spectral line shapes were separated by target factor analysis approximately as: two components for carbon, surface organic carbon and carbide; two components for oxygen, Zr oxide and SiO<sub>2</sub>; three Si components, SiO<sub>2</sub>, Si, and some intermediate oxidation state. The profile curves for both samples were scaled by approximate sensitivity factors. Solution composition was determined by ICP analysis by Galbraith Laboratories and confirmed by RBS analysis. Film thickness was determined by n&k analysis (n&k analyzer, n&k Technology, Santa Clara, Ca)<sup>6</sup> and confirmed by single wavelength ellipsometry. Electric properties were measured using backside contact with In/Ga and topside contact with a Hg probe or thermally evaporated Al dots. The two types of electrodes yield similar electrical response apart from the flat band shift due to the work function difference of the metals.

## **RESULTS and DISCUSSION**

X-ray diffraction (XRD) was performed at room temperature on 15, 25, 50, 75% ZSO and 15, 25% HSO binary oxides after annealing hot plate baked (350 °C 30 minutes in air) films at 500, 700, 800, 900, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen. A typical series of XRD diffraction patterns are shown in Figure 1 for 15% HSO. After annealing 15% HSO at 800 and 900 °C, only a broad absorption centered at 28° is observed, characteristic of amorphous SiO<sub>2</sub>, after annealing at 1000 °C, peaks attributable to tetragonal HfO<sub>2</sub> are observed, and after annealing at 1200 °C, peaks attributable to monoclinic HfO<sub>2</sub> are observed. Similar results were observed in the 15, 25, 50, 75% ZSO and 25% HSO films. Only a weak broad peak centered at ~28° characteristic of amorphous SiO<sub>2</sub> was observed in the X-ray diffraction spectra of the 15, 25, 50, 75% ZSO and 15, 25% HSO films annealed at 350-700 °C. After annealing at 800 °C, the tetragonal phase of ZrO<sub>2</sub> is observed in the spectra of 75% and 50% ZSO films. After annealing at 1000 °C, tetragonal ZrO<sub>2</sub> and HfO<sub>2</sub> are observed in the spectra of 25% and 15% ZSO and HSO films. After annealing 25% and 15% HSO films at 1100 and 1200 °C, respectively, monoclinic HfO<sub>2</sub> was observed. Tetragonal ZrO<sub>2</sub> or HfO<sub>2</sub> was only observed after annealing at  $\geq$  800 °C. No monoclinic ZrO<sub>2</sub> was observed in any of the ZSO films even after annealing at 1200 °C for 60 min. The annealing temperatures at which crystallized tetragonal and monoclinic ZrO<sub>2</sub> and HfO<sub>2</sub> are observed in XRD and FTIR spectra are listed in Table I.

Table I. Annealing temperatures at which crystallized tetragonal and monoclinic  $ZrO_2$  and  $HfO_2$  are observed in the XRD and FTIR spectra of ZSO and HSO films.

n/m: not measured, n/o: not observed.

$Zr_xSi_{1-x}O_y$ x=	$T_{\text{crystallization}} \text{ } ^\circ\text{C}$ tetragonal		$T_{\text{crystallization}} \text{ } ^\circ\text{C}$ monoclinic		$Hf_xSi_{1-x}O_y$ x=	$T_{\text{crystallization}} \text{ } ^\circ\text{C}$ tetragonal		$T_{\text{crystallization}} \text{ } ^\circ\text{C}$ monoclinic	
	XRD	FTIR	XRD	FTIR		XRD	FTIR	XRD	FTIR
0.15	1,100	900	>1200		0.15	1,000	900	1,200	1000
0.25	1,000	900	>1200		0.25	1,000	900	1,100	1000
0.5	800	800	>1200						
0.75	800	800	>1200						
1 <sup>7</sup>	450	n/m	550	n/m	1 <sup>8,18</sup>	n/o	n/m	550	n/m

As observed by XRD and in agreement with earlier bulk CSD aerogel results,<sup>7</sup> we have observed that combination of  $ZrO_2$  with silica ( $SiO_2$ ) in the ZSO films delayed crystallization of tetragonal  $ZrO_2$  from 450 °C to at least 800 °C, and that transformation of the tetragonal to the monoclinic phase was not observed even after annealing at 1200 °C for 60 minutes. No reports of HSO deposited by CSD are found in the literature. Silica free  $HfO_2$  has been prepared by CSD and crystallization of monoclinic  $HfO_2$  is observed after annealing at 550 °C.<sup>8,18</sup> In the 15 and 25% HSO films, we observe crystallization of tetragonal  $HfO_2$  before crystallization of monoclinic  $HfO_2$ . In agreement with the ZSO results, combination of  $HfO_2$  with silica in HSO films delays crystallization of  $HfO_2$ , and crystallization of the tetragonal phase is observed at lower temperatures than crystallization of the monoclinic phase. The presence of the tetragonal  $HfO_2$  or  $ZrO_2$  in the HSO or ZSO films at lower temperatures than the monoclinic phase might be attributable to several factors including anionic impurities, structural similarities between the amorphous and tetragonal phase, as well as particle size effects which imply that a critical particle size must be reached before the tetragonal-monoclinic transformation will occur.<sup>7</sup>

## FTIR

To gain a better understanding of the microstructural transformations occurring during annealing, FTIR spectra were collected from 15% (Fig. 3), 25% (Fig. 4), 50% (Fig. 5), and 75% (Fig. 6) ZSO and 15% (Fig. 7) and 25% (Fig. 8) HSO films annealed for 30 minutes in oxygen at 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen. The peaks in the ZSO and HSO spectra have been assigned according to the literature.<sup>7-16</sup> The broad band between 3700 and 3000  $cm^{-1}$  is assigned to O-H stretching vibrations. The band at 1630  $cm^{-1}$  is assigned to the H-OH bending vibration of adsorbed water in the film. The absorption bands centered at 1180, 1080, 810 and 460  $cm^{-1}$  are characteristic of a silica network: the bands at 1200 and 1070  $cm^{-1}$  are ascribed to the LO and TO components of the asymmetric stretch of the  $SiO_4$  unit, respectively and the absorption bands at 810  $cm^{-1}$  and 460  $cm^{-1}$  are attributed to skeletal network Si-O-Si symmetric stretching and bond bending respectively.

The FTIR spectra of the 75%, 50%, 25%, and 15% ZSO and 25% and 15% HSO films baked at 350 °C in air on a hot plate for 30 minutes are shown in Fig. 2. Weak absorption bands

between 3090 and 2800  $\text{cm}^{-1}$  associated with C-H stretch and absorption bands between 1500 and 1300  $\text{cm}^{-1}$  associated with C-H deformation are observed and attributed to residual organics in the film. As  $\text{ZrO}_2$  or  $\text{HfO}_2$  content is increased the intensity of the broad absorption bands centered at  $\sim 3500 \text{ cm}^{-1}$  associated with hydroxyl and the absorption bands at 1630  $\text{cm}^{-1}$  associated with adsorbed water increases. The increased adsorbed water at higher  $\text{ZrO}_2$  and  $\text{HfO}_2$  doping is most likely associated with the increased hydroxy content which increases with  $\text{ZrO}_2$  and  $\text{HfO}_2$  content. The increased hydroxy and adsorbed water content is most likely attributable to the disruption of the silica network by the  $\text{ZrO}_2$  and  $\text{HfO}_2$  doping resulting in increased terminal non-bridging sites.<sup>9</sup> A broad strong adsorption band is observed between 1200 and 810  $\text{cm}^{-1}$  and is composed of contributions from the LO and TO components of the asymmetric stretch of the  $\text{SiO}_4$  unit at 1180  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$ , a shoulder at  $\sim 970 \text{ cm}^{-1}$  assigned to Si-O-M (M is Hf or Zr)[7],<sup>9-11</sup> and a shoulder at  $\sim 880 \text{ cm}^{-1}$  assigned to Si-O $^-$  (where O $^-$  is a nonbridging oxygen ion, bonded to a proton).<sup>10,12</sup> A broad absorption band from 600-400  $\text{cm}^{-1}$  centered at  $\sim 430 \text{ cm}^{-1}$  is observed in all the films. The broadness of the band suggests a wide dispersal of vibrational states which is characteristic of an amorphous network. Contributions to the band are attributed to Zr-O<sup>16</sup> and Si-O vibrations.

As shown in Fig. 2,  $\text{HfO}_2$  was observed to be highly disruptive of the silica network. Even at relatively low  $\text{HfO}_2$  (15 and 25% HSO) concentrations,  $\text{HfO}_2$  disturbed the silica network as evidenced by the large OH and  $\text{H}_2\text{O}$  content in the films, the broad adsorption centered at  $\sim 1000 \text{ cm}^{-1}$  suggesting a greater contribution from Si-O-M stretches and a greater disruption of the silica network, and the absence of the 810  $\text{cm}^{-1}$  band attributed to skeletal network Si-O-Si symmetric stretching. In contrast, at low Zr concentrations (15% and 25% ZSO), the silica network was relatively unperturbed, as evidenced by the relatively low OH and  $\text{H}_2\text{O}$  content in the films, and the absorption bands centered at 1040  $\text{cm}^{-1}$  suggesting a greater contribution from  $\text{SiO}_4$  stretching and less disruption of the silica network. Further support for less disruption of the silica network in the 15% and 25% ZSO films is provided by the weak absorption band observed at 810  $\text{cm}^{-1}$  assigned to skeletal network Si-O-Si symmetric stretching which is only observed in the 15% and 25% ZSO film spectras.  $\text{ZrO}_2$  is also disruptive of the silica network at higher concentrations. The silica network was greatly disturbed in the 75% and 50% ZSO as evidenced by the large OH and  $\text{H}_2\text{O}$  content in the films, the broad adsorption band centered at  $\sim 1000 \text{ cm}^{-1}$ , and the absence of the 810  $\text{cm}^{-1}$  band.

A progressive change in the FTIR spectrum is observed as the annealing temperature is increased to 500 and 700  $^\circ\text{C}$  (Fig. 3-8). Absorption bands attributed to hydroxyl and adsorbed water in films are observed to decrease in intensity and bands associated with residual organics in the films are absent. As the anneal temperature is increased, the center of the strong adsorption band between 1200 and 810  $\text{cm}^{-1}$  shifts to higher wave numbers and the contributions from the shoulders at 970 and 880  $\text{cm}^{-1}$  diminishes. Little change is observed in the broad absorption band between 600 and 400  $\text{cm}^{-1}$ .

Crystallization/phase separation of the ZSO and HSO films can be defined by FTIR as well as by X-ray diffraction. As shown in Fig. 3-8, upon crystallization/phase separation, a narrowing of the absorption band between 1200-800  $\text{cm}^{-1}$  and an upward shift of the center to  $\sim 1060 \text{ cm}^{-1}$  is observed with most of the absorption loss occurring at or below 1000  $\text{cm}^{-1}$  mostly from diminishment of the two shoulders at 970 and 880  $\text{cm}^{-1}$ . Also, the weak absorption band at 810  $\text{cm}^{-1}$  is observed in the 75% and 50% ZSO and 25% and 15% HSO spectra after crystallization/phase separation. Concurrently, a narrowing of the absorption band between

600-400  $\text{cm}^{-1}$  and an upward shift of the center from  $\sim 430 \text{ cm}^{-1}$  to  $\sim 460 \text{ cm}^{-1}$  is observed. The band centered at  $\sim 460 \text{ cm}^{-1}$  is composed of contributions from two bands one at  $480 \text{ cm}^{-1}$  characteristic of tetragonal  $\text{ZrO}_2$  and one at  $460 \text{ cm}^{-1}$  characteristic of Si-O-Si. The narrowing of the absorption bands and shifting of the peak position are presumably arising from crystallization and phase separation of tetragonal  $\text{ZrO}_2$  and  $\text{HfO}_2$  within the silica network, and a consolidation or sintering of the film. Similar changes in the FTIR spectra of ZSO have been reported previously.<sup>17,20</sup>

As determined by FTIR (using the criteria of a 10-20  $\text{cm}^{-1}$  peak shift and concurrent peak narrowing), this crystallization/phase separation occurs at 800 °C for 75% ZSO, 50% ZSO, and at 900 °C for 25% HSO, 15% HSO, 15% ZSO and 25% ZSO. With the exception of the 75% and 50% ZSO films, the crystallization/phase separation is observed at lower temperatures in the FTIR spectra than the X-ray diffraction spectra. The results are summarized in Table 1.

Additional changes are observed in the FTIR spectra in films annealed at temperatures above the crystallization/phase separation temperature (Fig. 3-8). As the anneal temperature is increased above the crystallization/phase separation temperature, the strong absorption band between 1200 and 810  $\text{cm}^{-1}$  continues to narrow and the center to shift to 1080  $\text{cm}^{-1}$ . The band at 810  $\text{cm}^{-1}$  is observed to increase and is indicative of sintering of the film via formation of additional Si-O-Si bonds by dehydration-condensation reactions. The band between 500 and 400  $\text{cm}^{-1}$  continues to narrow and the center to shift to 460  $\text{cm}^{-1}$ . In all of the films annealed at 1200 °C a weak absorption is observed at 935  $\text{cm}^{-1}$  and is attributed to Si-O-M vibrations and is indicative of sintering of Si-O-M bonds. In the ZSO films, a weak absorption band between 650 and 500  $\text{cm}^{-1}$  is observed, centered at 580  $\text{cm}^{-1}$  and is attributed to Zr-O vibrations of tetragonal  $\text{ZrO}_2$  in the  $\text{ZrO}_2$  rich phase.<sup>7,11,12</sup> The 15% and 25% HSO films have absorption bands attributable to monoclinic  $\text{HfO}_2$ <sup>16</sup> at 749, and 420  $\text{cm}^{-1}$  which are not observed in the ZSO films.

RBS and AES analysis was conducted on two 75% ZSO films one annealed at 900 °C and the second annealed at 1100 °C for 30 minutes. RBS analysis found that the films are approximately 1000 Å thick with a possible interfacial  $\text{SiO}_2$  layer between ZSO and Si and have an atomic percentage composition of 25% Zr, 0.3% Hf, 8% Si, 66.7% O. AES was conducted to confirm formation of an interfacial  $\text{SiO}_2$  layer. The AES analysis found that a 15nm or 20 nm  $\text{SiO}_2$  interface was observed between the ZSO and Si substrate, for the 900 °C and 1100 °C annealed films, respectively. Both samples contained C in a carbide like state, but the film annealed at 900 °C had 12 times more than the film annealed at 1100 °C. A very low level of N ( $\ll 1\%$ ) was detected in both films which possibly resulted from diffusion of N from the  $\text{SiO}_x\text{N}_y$  interface.

Dielectric constant was measured relative to  $\text{ZrO}_2$  content and annealing temperature of the films. Plotted in Figure 9 is the measured dielectric constant of 25%, 50% and 75% ZSO films annealed at 700 °C, 900 °C and 1100 °C for 30 minutes. Also plotted in Figure 9 is the annealing temperatures at which crystallized tetragonal  $\text{ZrO}_2$  is observed in the XRD spectra of ZSO films. A slightly higher dielectric constant was observed at lower annealing temperatures for the 25, 50 and 75% ZSO films. The slightly higher dielectric constant observed at lower annealing temperatures might be related to microstructural aspects of the ZSO films. One possibility is that the additional Si-O-Zr bonds present in non-phase separated ZSO are contributing to a larger dielectric constant. As the annealing temperature is increased above the crystallization/phase separation temperature, the dielectric constant of the films decreases and the intensity of the 950  $\text{cm}^{-1}$  FTIR peak attributed to Si-O-Zr also decreases. The decreased dielectric constant and decreased FTIR intensity is consistent with loss of Si-O-Zr bonds and phase separation into  $\text{ZrO}_2$

rich and SiO<sub>2</sub> rich regions within the film. Additionally, the dielectric constant is observed to increase with increasing ZrO<sub>2</sub> content, as is the intensity of the 950 cm<sup>-1</sup> FTIR peak, consistent with additional Si-O-Zr bonds.

As shown in Figure 9, in all cases, the dielectric constant is less than the linear combination of ZrO<sub>2</sub> and SiO<sub>2</sub> dielectric constants. The Clausius-Mossotti equation which describes a relation between the polarizability of atoms or ions and the macroscopic dielectric constant of an isotropic medium<sup>19</sup> seems to fit the experimental data nicely. A simple capacitor model for a phase separated system which assumes that individual components have a size that is much smaller than the film thickness, such that their respective capacitance can be considered to be in series produces a very similar curve to the Clausius-Mosotti and also fits the data. The Clausius-Mossotti equation and a simple capacitor model for a phase separated system predict that to achieve a dielectric constant larger than 10 in the ZSO films at least a 70% doping level of Zr is necessary.

## CONCLUSIONS

Crystallization/phase separation of ZrO<sub>2</sub> and HfO<sub>2</sub> in ZSO and HSO films was observed to be concentration dependent. Combination of ZrO<sub>2</sub> and HfO<sub>2</sub> with SiO<sub>2</sub> in the ZSO and HSO films delayed the crystallization of ZrO<sub>2</sub> and HfO<sub>2</sub> from 450 °C to at least 800 °C and stabilized the tetragonal phase. Transformation from the tetragonal to monoclinic phase was observed in HSO films but not in ZSO films even after annealing at 1200 °C for 60 minutes.

ZrO<sub>2</sub> and HfO<sub>2</sub> were observed to act as silica network modifiers. HfO<sub>2</sub> was observed to be highly disruptive of the silica network, as evidenced by the FTIR spectra of the films annealed below the crystallization/phase separation temperature. The ZSO and HSO films are metastable and were observed to undergo progressive microstructural changes in the FTIR after each of the annealing steps. Crystallization/phase separation of the films was accompanied by the appearance of bands attributable to a silica network and bands attributable to ZrO<sub>2</sub> and HfO<sub>2</sub> in the FTIR spectra.

A slightly higher dielectric constant was observed at lower annealing temperatures for the 25, 50 and 75% ZSO films which may be related to additional Si-O-M bonds contributing to a larger dielectric constant in the non-phase separated films. In all cases, the dielectric constant was observed to be less than the linear combination of ZrO<sub>2</sub> and SiO<sub>2</sub> dielectric constants. The Clausius-Mossotti equation and a simple capacitor model for a phase separated system was observed to fit the data with the prediction that to achieve a dielectric constant larger than 10 doping concentrations of ZrO<sub>2</sub> would have to be greater than 70%. However, we have shown that ZSO films with 50% or greater ZrO<sub>2</sub> content crystallize at 800 °C and would not be likely to survive an implant activation anneal at 1000 °C.

## ACKNOWLEDGEMENTS

The authors acknowledge Horatio Wildman for AES analysis and Keith Pope for RBS analysis.

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## FIGURES

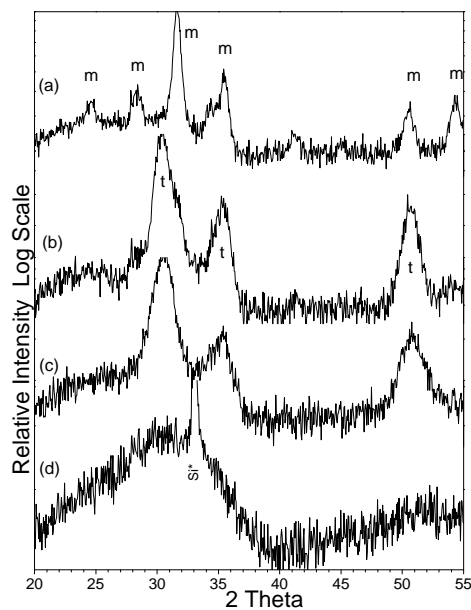


FIG. 1. X-ray diffraction pattern of 15% HSO film furnace annealed at (a) 1200 °C 60 minutes, and (b) 1100, (c) 1000, 900, and (d) 800 °C for 30 minutes in flowing oxygen; m: monoclinic phase of  $\text{HfO}_2$ , t: tetragonal phase of  $\text{HfO}_2$ .

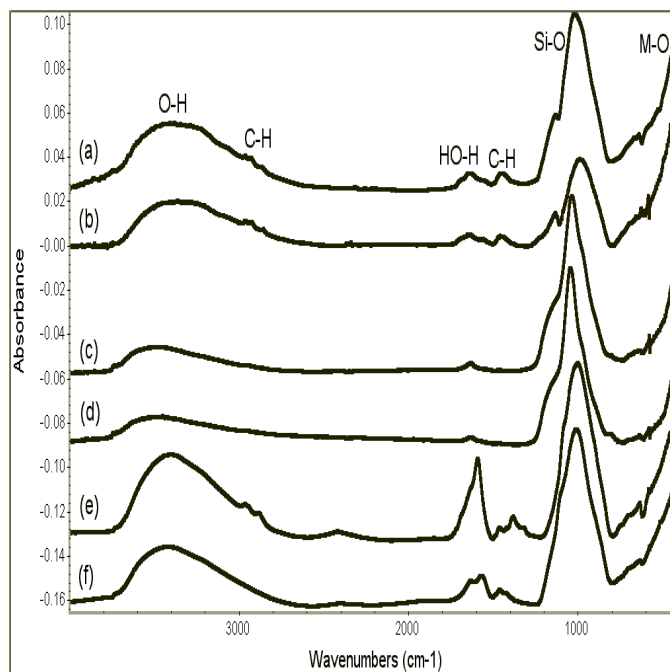


FIG. 2. FTIR spectra of (a) 75% ZSO, (b) 50% ZSO, (c) 25% ZSO, (d) 15% ZSO, (e) 25% HSO, and (f) 15% HSO films after hot plate bake at 350 °C for 30 minutes in air.

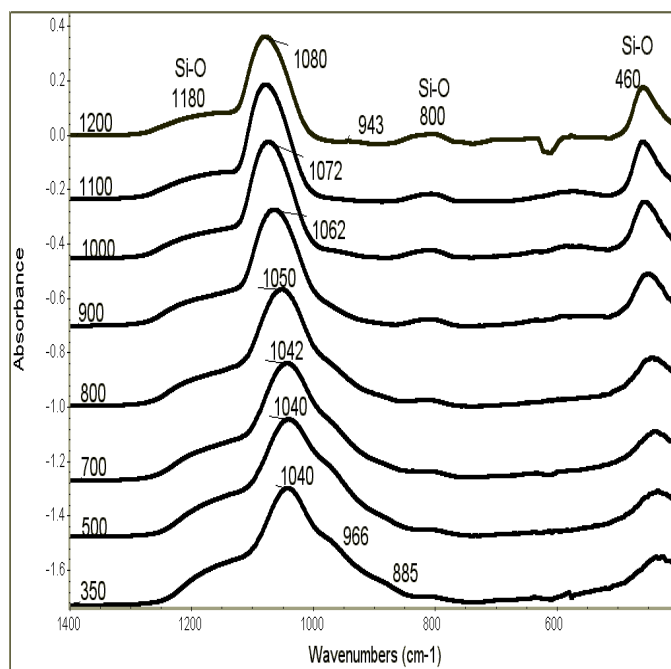


FIG. 3. FTIR spectra of 15% ZSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

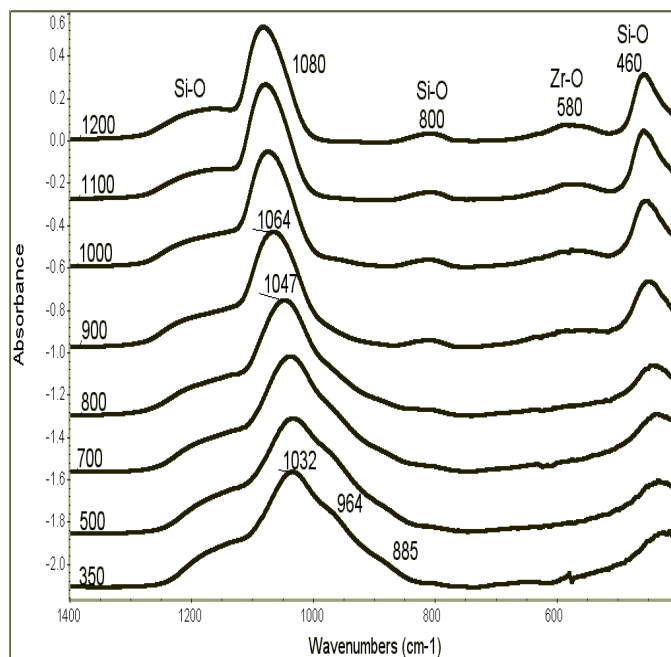


FIG. 4. FTIR spectra of 25% ZSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

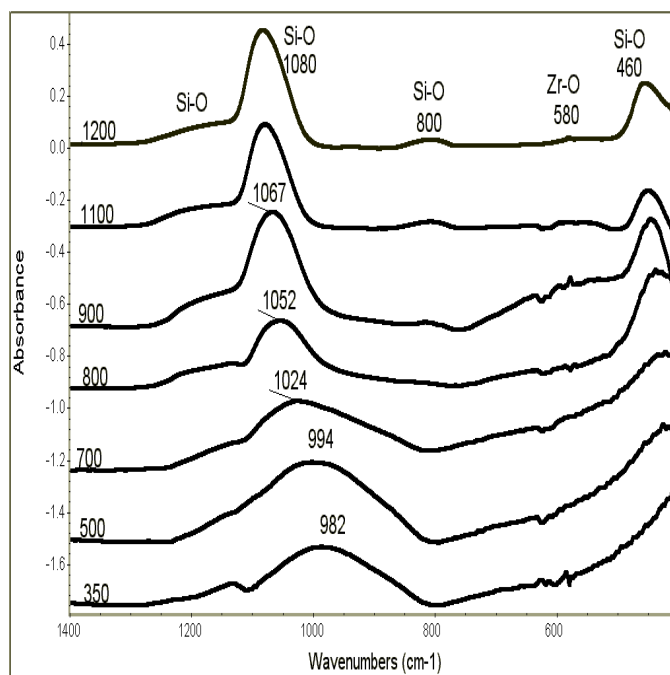


FIG. 5. FTIR spectra of 50% ZSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

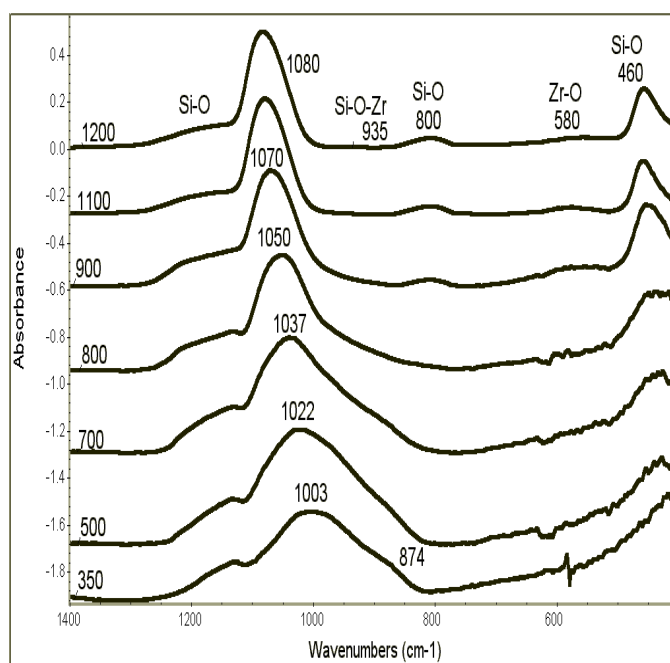


FIG. 6. FTIR spectra of 75% ZSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

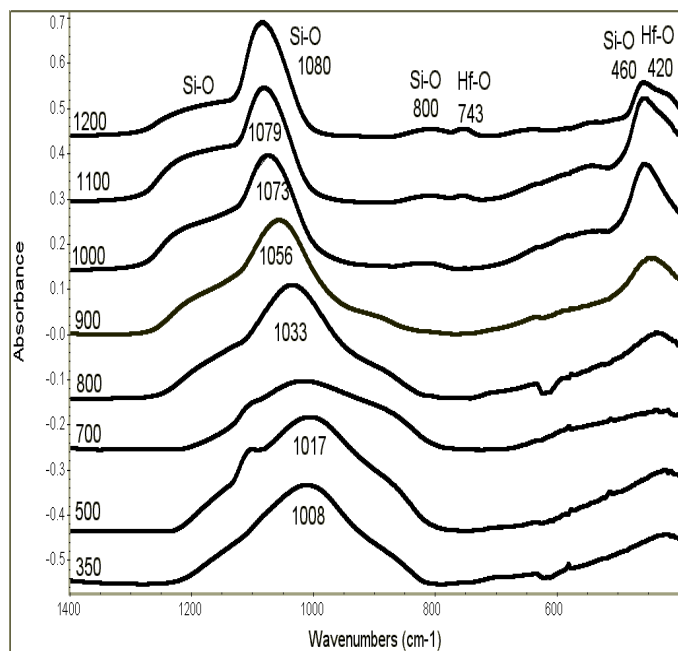


FIG. 7. FTIR spectra of 15% HSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

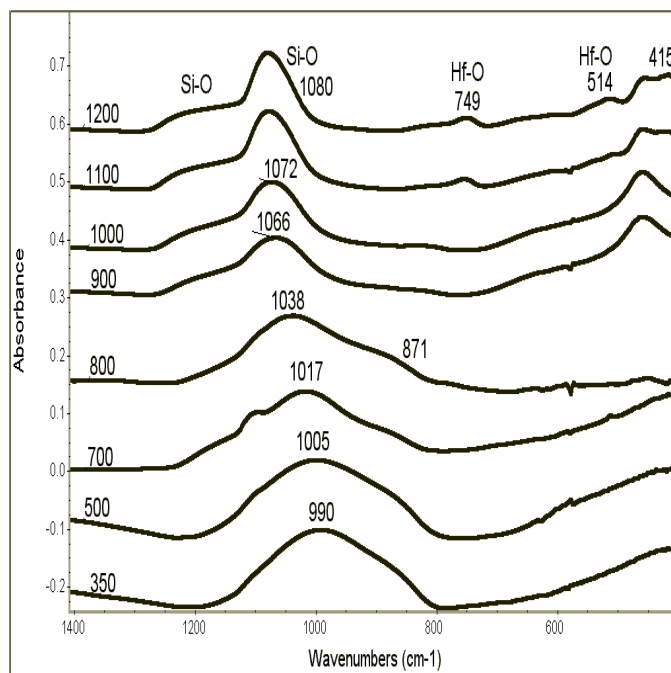


FIG. 8. FTIR spectra of 25% HSO films after annealing at 350, 500, 700, 800, 900, 1000, 1100 °C for 30 minutes and 1200 °C for 60 minutes in flowing oxygen.

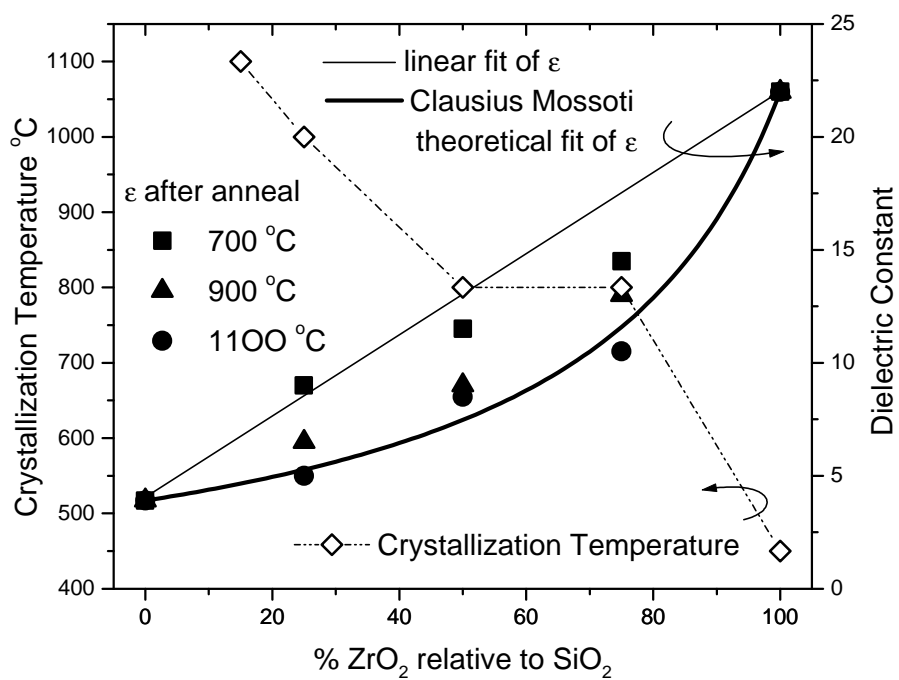


FIG. 9. Plot of dielectric constant and crystallization/phase separation temperature vs. %ZrO<sub>2</sub> in 100 nm ZSO films for 25%, 50% and 75% ZSO, annealed at 700, 900, and 1100 °C for 30 minutes in flowing oxygen.



