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Electrical and Optical Properties of HfO_2–Nd_2O_3 Dielectric Films

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Abstract—HfO_2–Nd_2O_3 dielectric films were produced by vacuum electron-beam evaporation, and their electrical properties were studied as a function of composition. *C–V* measurements were used to calculate parameters of the films and semiconductor–dielectric interfaces. The films exhibit high thermal stability in electric fields. The effect of stabilizing treatment on the optical properties of the films is examined. The films are believed to have great potential for use in thin-film electroluminescent devices and thermally stable capacitors.

INTRODUCTION

The ability to produce high-quality dielectric films possessing good optical and electrical properties is crucial to microelectronics.

There is currently considerable interest in films based on binary systems. By varying film composition and deposition conditions, the required electrical characteristics can be achieved with a high degree of accuracy and stability. In this context, much promise is shown by HfO_2–R_2O_3 (R = rare-earth metal) films, since it is now well established that the cubic structure of hafnia can be stabilized by additions of rare-earth oxides [1] to give a highly stable phase.

In this paper, we report the physical properties of thin HfO_2–Nd_2O_3 dielectric films.

EXPERIMENTAL

HfO_2–Nd_2O_3 dielectric films were deposited by vacuum electron-beam evaporation onto glass, sapphire, and quartz substrates. In each run, films were deposited simultaneously onto substrates for optical measurements and those for metal–insulator–metal (MIM) and metal–insulator–semiconductor (MIS) structures. The deposition conditions ensuring the best performance characteristics of the films were identified earlier [2, 3]. Electrical contacts to the structures were made by thermal evaporation of aluminum in a vacuum of 5×10^{-5} Pa.

In capacitance and dielectric loss measurements, we used E7-8 and E7-11 multimeters. Optical studies were carried out with a KSVU-23 computer-controlled spectrometric system.

RESULTS AND DISCUSSION

The dielectric properties of the HfO_2–Nd_2O_3 films studied are summarized in Table 1. These data were obtained as averages over six substrates, with 120 MIM structures on each.

The films were found to possess high dielectric permittivity, low loss tangent, high dielectric strength, and high thermal stability (Table 1). The dielectric properties of the films could be improved and stabilized by heat treatment at 300°C in an oxygen atmosphere. After heat treatment, the films showed high stability of properties in the frequency range 1 kHz to 1 MHz. Thus, our results indicate that HfO_2–Nd_2O_3 films are candidate materials for thermally stable thin-film capacitors. Note, however, that the temperature coefficient of permittivity in HfO_2–Nd_2O_3 films is larger than that in HfO_2 films.

High-frequency capacitance–voltage (*C–V*) and capacitive transient measurements were used to calculate the flat-band voltage V_{FB}, effective charge density Q_{FB} in the dielectric, the effective carrier lifetime τ_g, and the density of surface states N_{SS} at the semiconduc-

Table 1. Dielectric properties of HfO_2–Nd_2O_3 films

Batch no.	Weight percent Nd_2O_3	ε (1 kHz)	$\tan\delta$ (1 kHz)	E_{br}, MV/cm (f = 50 Hz)	TC of ε, 10^{-4} K^{-1}
1	0.00	18	0.030	3.6	2.8
2	7.75	18	0.025	3.4	3.0
3	15.06	17	0.018	3.6	3.0
4	21.98	26	0.005	5.3	3.0
5	25.00	26.5	0.004	6.4	2.7
6	28.52	27	0.003	7.0	2.5
7	34.73	27	0.003	6.4	2.9
8	51.55	17	0.008	1.7	8.2
9	61.48	16	0.012	1.6	12.3
10	100.00	15	0.015	1.3	30.2

[†] Deceased.

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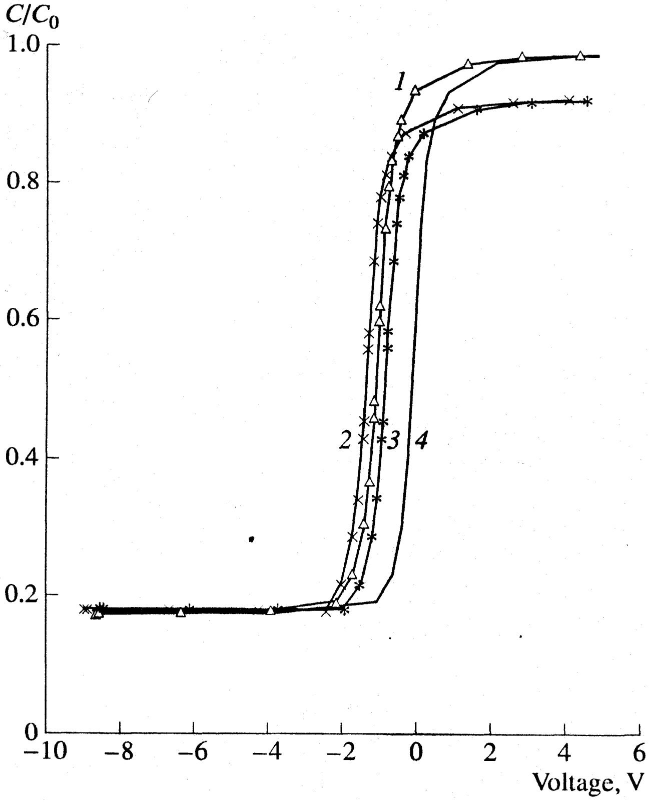

Fig. 1. C–V characteristics of MIS structures based on HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) films: (*1*) before TET; (*2*, *3*) after TET with the gate biased positively and negatively, respectively, followed by annealing; (*4*) ideal characteristics.

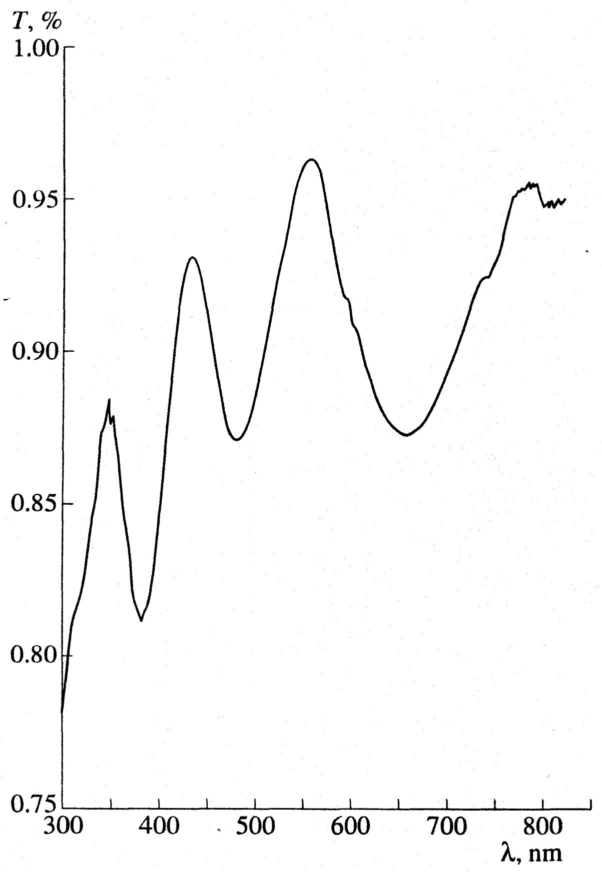

Fig. 2. Transmission spectrum of the HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) film.

tor–dielectric interface [4]. The results are summarized in Table 2.

To assess the contributions of different mechanisms to the measured surface-charge density, MIS structures were heated to 200°C over a period of 1 h with the gate biased positively or negatively at a field strength of 10^4–10^5 V/cm (thermoelectric treatment, TET).

Figure 1 displays typical C–V characteristics of MIS structures with an HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) layer. As follows from these data, TET leads to a decrease in capacitivity by 5–7%, which seems to be caused by the burn-out of "current channels" (high-conductivity regions) and reoxidation of the rare-earth atoms reduced upon deposition. As a result, the stability of the dielectric rises, and its electrical properties become more uniform. By adjusting the TET conditions, the surface-charge density can be varied by ±25%.

A typical transmission spectrum of the dielectric films is shown in Fig. 2. The optical characteristics were calculated as described in [5]. The results are summarized in Table 3. As follows from these data, the films are transparent and have a high refractive index throughout the visible region.

Table 2. Electrical properties of MIS structures based on HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) dielectric layers

Conditions	As-prepared	TET-I without HT	TET-II without HT	TET-I + HT	TET-II + HT
V_{FB}, V	−1	−1.3	−1.27	−1.15	−0.94
Q_{FB}, C/cm^2	43.7×10^{-8}	5.7×10^{-8}	5.5×10^{-8}	5.5×10^{-8}	4.1×10^{-8}
Hysteresis, V	0.6	0.3	0.2	0.25	0.2
N_{SS}, eV^{-1}/cm	6.2×10^{11}	6.5×10^{12}	4.1×10^{12}	8.5×10^{11}	5.5×10^{11}
τ_g, μs	1.04	3.9	0.92	2.2	1.8

Note: HT = heat treatment; (I) negatively biased gate; (II) positively biased gate (see text).

Table 3. Optical characteristics of HfO_2–Nd_2O_3 films as a function of composition

Weight percent Nd_2O_3	λ, nm	n_2	k	Substrate
0	384	1.79		Glass, quartz
	470	1.75	0.095	
	624	1.69	0.12	
	800	1.61	0.08	
15	452	1.6		Glass, quartz
	698	1.72	0.12	
25	434	1.74		Glass, quartz, sapphire
	542	1.63	0.075	
	698	1.58	0.07	
	864	1.57	0.065	
28.5	366	1.64		Glass, quartz
	538	1.73	0.1	

Note: n_2 is the refractive index, and k is the absorption coefficient.

Table 4. Optical characteristics of HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) films after different treatments

Treatment	λ, nm	n_2	k	Substrate
HT in vacuum at 250°C	434	1.75		Quartz, Sapphire
	542	1.66	0.1	
	698	1.56	0.1	
	864	1.53	0.11	
HT in air at 250°C	434	1.75		Quartz
	542	1.66	0.1	
	698	1.57	0.11	
	864	1.54	0.12	
HT in air at 500°C	434	1.63		Quartz
	542	1.61	0.11	
	698	1.56	0.12	
	864	1.52	0.12	
Boiling in water for 1 h	434	1.76		Quartz, Glass
	542	1.74	0.13	
	698	1.71	0.16	
	864	1.69	0.19	

HfO_2–Nd_2O_3 films are possible candidates for use in thin-film electroluminescent devices (TFELDs). The dielectric films employed in TFELDs must have optical properties that are highly stable upon exposure to water or elevated temperatures, since the characteristics of such devices are typically stabilized by heat treatment at about 500°C.

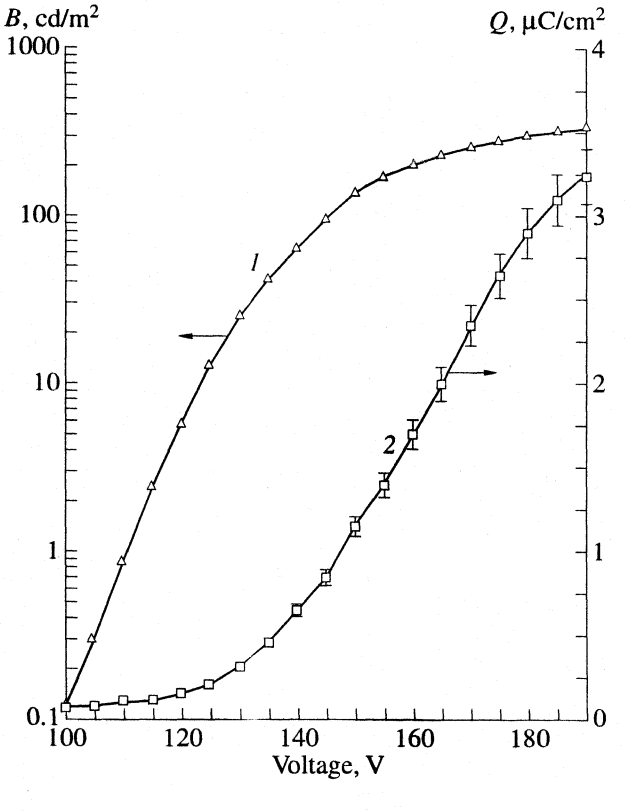

Fig. 3. (*1*) Voltage–light and (*2*) voltage–charge characteristics of thin-film electroluminescent devices.

To study thermal influences on the performance characteristics of the films, they were annealed in air or in a vacuum of 5 × 10^{-5} Pa. Resistance to water attack was assessed by boiling optical structures in water for 1 h. After that, the transmission spectra were remeasured and the optical characteristics recalculated. The results are displayed in Table 4.

Comparison of the data given in Tables 3 and 4 demonstrates that heat treatments in air and vacuum have essentially identical effects on the optical properties of the films. Technological treatment causes no significant changes in the optical properties of the films, except for boiling, which reduces the dispersion of the refractive index. At the same time, repeat annealing at 500°C after boiling leads to the recovery of optical properties, which testifies to the high stability of HfO_2–Nd_2O_3 films.

HfO_2–Nd_2O_3 (25 wt % Nd_2O_3) films were used to fabricate TFELDs of the metal–insulator–semiconductor–insulator–metal (MISIM) type. The voltage–light and voltage–charge characteristics of these structures are shown in Fig. 3. The TFELDs feature a low threshold voltage, high brightness, and sizable dielectric strength. The use of HfO_2–Nd_2O_3 dielectric layers in the TFELDs ensures a decrease in threshold voltage by a factor of 1.5–2 in comparison with devices in which conventional insulators such as Y_2O_3 or Al_2O_3 are employed. Note that the dielectric layers were deposited by the procedure compatible with those used to deposit ZnS semiconductor layers.

CONCLUSION

The advantageous combination of dielectric, electrical, and optical properties makes HfO_2–Nd_2O_3 dielectric films potential materials for thermally stable capacitors and information display systems.

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