Size-dependent anomalous dielectric behavior in La$_2$O$_3$ : SiO$_2$ nano-glass composite system

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Abstract. An intriguing anomalous dielectric behavior is observed in nanoparticle (NP) La$_2$O$_3$ : SiO$_2$ nano-glass composite system synthesized via sol-gel route at different calcination temperatures. Temperature dependent dielectric properties exhibit a notable dielectric broadening, indicating of diffuse phase transition with high $\varepsilon'$, quite different from and much higher than pure bulk La$_2$O$_3$ and SiO$_2$. We postulate such dielectric effect in the context of the oxygen vacancies of the rare earth oxide nano-glass composite, where lattice strain related with NPs and their size plays a vital role. Such a material might be treated as a potential candidate to solve the problem of devices miniaturization.

1. Introduction
Unacceptable leakage currents have imposed severe constraints in downscaling of microelectronic devices. Even while having the same thickness of SiO$_2$, the “new” high-$k$ dielectric material (greater than that of SiO$_2$ ($k\sim3.9$)) can provide a substantially greater physical thickness (defined as equivalent oxide thickness (EOT)) to solve the technical problem of direct tunneling leakage current. Recent reports of giant dielectric constant have directed considerable attention to several new material systems, such as perovskite-related materials ACu$_3$Ti$_4$O$_{12}$ (A = Ca, Bi$_{2/3}$, Y$_{2/3}$, La$_{2/3}$) [1,2], La$_{2/3}$Li$_x$Ti$_{1-x}$Al$_x$O$_3$ [3], Nd$_3$O$_3$ doped (1-x)Bi$_{0.8}$Na$_{0.2}$TiO$_3$-xBi$_{0.8}$K$_{0.2}$TiO$_3$ [4], Fe-containing complex perovskites A(Fe$_{1/2}$B$_{1/2}$)O$_3$ (A=Ba, Sr, Ca; B=Nb, Ta, Sb) [5,6], nonperovskite material Li$_{0.05}$Ti$_{0.02}$Ni$_{0.93}$O (LTNO) [7], percolative BaTiO$_3$-Ni composites [8], electron-doped manganites Ca$_{1-x}$La$_x$MnO$_3$ and hole-doped insulators La$_3$Cu$_{1-x}$Li$_x$O$_4$ and La$_{3.8}$Sr$_{0.2}$NiO$_4$ [9-11]. However, these types of materials possess compositional variations, structural inhomogeneities, or phase heterogeneities in physical scale from micron or submicron range to the atomic level. Therefore, searching for alternative materials containing single-valence ions with phase stability is highly desirable. Recently, there has been a trend of development of oxide nanoparticles (NPs) in a nonmagnetic dielectric matrix (like SiO$_2$) to tailor desired magnetic, dielectric, and other properties by altering the type and concentration of the dopant ions. Among the various oxides, we have attempted to grow nanosized lanthanum oxide particles in inorganic silica by adopting a sol-gel method. La$_2$O$_3$ possesses appealing properties such as a large conduction band offset over 2 eV [12], a large band gap ($E_g$~5.4 eV) and good thermodynamic stability with silicon that prevents the formation of silicides and roughed surfaces [13]. The sol-gel process provides a convenient way to tailor rare earth oxide NPs of nearly uniform sizes and facilitates homogeneous dispersion of these metal oxide NPs in the silica matrix. In the present instance, the
doping level is chosen as 0.5 mol%, and La$^{3+}$-doped SiO$_2$ glass is subjected to calcination at various temperatures up to 900 °C.

2. Experimental Details

Lanthanum oxide doped silica gel was prepared from tetraethylorthosilicate (TEOS) and dopants; namely, lanthanum salt having 0.5 mol% concentration following essentially the method developed by Sakka and Kamiya [14]. The process was based on hydrolysis of precursors TEOS and subsequent condensation of hydrolyzed TEOS in a medium containing a hydroalcoholic solution of lanthanum salt. The sol-gel derived dried monolithic transparent gel samples were calcined at different temperatures 700°, 800°, and 900 °C (henceforth referred as La05-7, La05-8, and La05-9, respectively).

An ultrahigh-resolution TEM (Model: JEM-3010, JEOL) was employed to analyze the detailed structure of samples. The magnetic hysteresis measurements were performed in a SQUID magnetometer (Model: MPMS-XL, Quantum Design) with temperatures varying from 2 to 300 K, equipped with a superconducting magnet producing fields up to ±6T. The dielectric measurements were carried out with LCR meter (Model E4980A, Agilent) in conjunction with laboratory built cryostatic arrangement integrated to the physical properties measurement system (Model: 6000, Quantum Design).

3. Results and Discussion

3.1. TEM and magnetization study

The TEM image of the powder specimen La05–7 (inset of figure 1) shows nearly spherical NPs of La$_2$O$_3$ (~3 nm) embedded in the glass matrix. The data obtained for the temperature dependence of the dc mass magnetization (ZFC and FC) of La05-7 samples in the presence of an applied dc magnetic field of 500 Oe in the 5–300 K temperature range are graphically represented in figure 1. Maxima in the ZFC mass magnetization curve for the sample La05-7 is obtained at 83 K. This characteristic temperature is often referred to as the blocking temperatures ($T_B$), typical of this measurement technique. The occurrence of $T_B$ has revealed the presence of the superparamagnetic phase of La$_2$O$_3$ NPs in these samples. From the observed continuous increase in FC magnetization with the lowering of the temperature below $T_B$, it appears that La$_2$O$_3$ NPs have FM-like ordering below the irreversibility temperature. For the La05-7, ZFC curve starts to rise from 40 K with the further lowering of the temperature (figure 1). Such an increase in magnetic moment may have originated from the paramagnetic contribution from a small number of isolated La$^{3+}$ ions present in the samples.

3.2. Impedance spectroscopy

Figure 2 illustrates the temperature dependent of the real part of relative dielectric permittivity ($\varepsilon'$) of
La05-7 at several selective frequencies in the absence of magnetic field. The shape of the curves, all with a well-defined maxima at $T_m \approx 340$ K, are notably different from those observed in classical relaxor ferroelectrics, which are characterized by a broad dielectric permittivity exhibiting maxima with frequency dispersion. However, such a dielectric broadening around $\varepsilon'_m$ (maximum value of $\varepsilon'$) is indicative of a diffuse phase transition (DPT) [15-17] with high $\varepsilon'$, quite different from and much higher than that of pure bulk La$_2$O$_3$ ($\varepsilon' \approx 12$) and of SiO$_2$ ($\varepsilon' \approx 3.9$). The space-charge or interfacial polarization may be operative in this specimen at temperatures above $T_m$. However, the enhancement of dielectric permittivity occurs even at temperatures below $T_m$ (~200-300 K). Therefore, any space-charge or interfacial polarization as the source of the enhancement of dielectric permittivity below $T_m$ is not evident. Beside $T_m$, another kink $T_o \approx 240$ K is also visible. The $\varepsilon'$-$T$ of La05 at different calcined temperatures are elucidated in the inset of figure 2. It is obvious that $\varepsilon'$ value is larger with the lower calcined temperature sample (i.e., particle size dependent effect). Interestingly, as crystal size increases with higher annealing temperatures, the $\varepsilon'$ value, and hence the associated DPT behavior, decreases.

To shed more light on the role of the relaxation dynamics, figure 3 depicts the temperature dependence of the dielectric loss tangent, $\tan \delta$ for various frequencies. The main feature observed is the appearance of maxima (~225 K) with low dielectric loss of $\tan \delta$-$T$. The peaks shift to higher temperatures as the frequency increases. The most important outcome of this analysis is complemented by reading off loss-peak positions in the temperature-frequency-dependent plot. In the inset of figure 3, the resulting temperature dependence of $\tau$ is shown in an Arrhenius representation. Near $T_m$, thermally activated behavior, $\tau = \tau_0 \exp(E_a / kT)$, is observed with an energy barrier $E_a$ of about 0.53 eV. These experimental facts suggest that the dielectric relaxation process might be closely associated to the presence of thermally activated oxygen vacancies. Thermally activated reorientation of dipole moment...
via the vacancy jumping (or, more correctly, the oxygen ion jumping through the oxygen vacancy) has been suggested as the origin of the dielectric relaxation with activation energy ~0.6–1.2 eV \[18,19\]. The NP La$_2$O$_3$ : SiO$_2$ arises spontaneously (self-organized) in a natural way with almost equal size and separation. Observation demonstrates the dielectric properties of NPs are seemingly an intrinsic feature of this new family and are independent of sample dimension. Moreover, the particle size, separation and concentrations of the La$_2$O$_3$ NP contributing to the permittivity are easily controllable with annealing temperature and doping concentration. This NP-glass composite system may be a promising high-$k$ gate dielectrics due to its high dielectric constant, single-stage process in air at moderate temperature, and good compatibility with modern microelectronics processing techniques.

4. Conclusions

In conclusion, we have successfully synthesized self-organized La$_2$O$_3$ NP with almost equal size (2–4 nm) and separation embedded in SiO$_2$ glass matrix by the sol-gel method. Properly annealed sol-gel glass shows an interesting colossal enhancement of dielectric constant along with diffuse phase transition around room temperature. The observed diffuse phase transition is related to the thermally activated oxygen vacancies, decreasing with higher calcination temperatures. The present study on highly stable high-$k$ material might provide an alternative route to seek a potential candidate for device applications.

Acknowledgements

This work was supported by National Science Council, Taiwan under Grant No. NSC 97-2112-M-110-005-MY3.

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