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Fabrication of $LaAlO_3$ film by sol-gel process with corresponding inorganic*

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Abstract: Well-cubic perovskite lanthanum aluminate ($LaAlO_3$) film on (110) silicon substrate was fabricated by sol-gel method with corresponding inorganic salts. Lanthanum acetate and aluminum acetate glacial acetic acid solutions were prepared via ligand exchange starting from lanthanum nitrate hexahydrate and aluminum nitrate hexahydrate after being refluxed. $(CH_3CO)_2O$ removed nitrates and the crystallized H_2O completely, acetylacetone (AcAc) was partially bidentated with metallic ion of the metallic acetates and formed $La(OAc)_{3-x}(AcAc)_x$, which were hydrolyzed into $La(AcAc)_{3-x}(OH)_x$ by adding 10 ml 0.4% methyl cellulose (MCL) solution. The $La(AcAc)_{3-x}(OH)_x$, polymerizing and combining with MCL, formed the $LaAlO_3$ sol precursor with heteropolymeric structure and formed film easily. The epitaxial $LaAlO_3$ film on Si(110) substrate was crystallized after being annealed in thermal annealing furnace for 650–750 °C/30 min. The morphologies and microstructures were characterized. The refractive index of the LAO film was 1.942 to 2.007; the dielectric constant and the dissipation factors were estimated to be 23–26 and 2.1×10^{-4} – 2.4×10^{-4} respectively.

Key words: Sol-gel method, $LaAlO_3$ film, Dielectric constant
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INTRODUCTION

The scaling down of silicon integrated circuits has pushed conventional SiO_2 gate films close to its physical limit. When the SiO_2 physical thickness become thinner than ~3 nm, direct tunneling through the dielectric barrier dominates the leakage current (Xiang *et al.*, 2003). A high-k dielectric material $LaAlO_3$ (LAO) to solve this problem has attracted much attention for fabrication of advanced complementary metal-oxide-semiconductor field-effect transistors (CMOS-FETs) with high current drivability, while the suitable dielectric constant and a low dielectric loss in the microwave region and a small lattice mismatch with a high Tc superconductor YBCO (Xu and Shi, 2003) make the LAO serve as substrate of the superconducting thin film for the development of ultrafast sensitive heterodyne receivers of electro-magnetic radiation (Il'in and Siegel, 2002). Furthermore, The LAO film is also important in a ferroelectric-gate FET (Park and Ishiwara, 2003) as a buffer layer, inserted between a ferroelectric thin film and an Si substrate [metal-ferroelectric-insulator-semiconductor (MFIS) structure]. In this application, the role of the buffer layer is to prevent interdiffusion of constituent elements such as Pb and Bi in the ferroelectric film into an Si substrate, and in order to keep the data retention time of the memory FET long, it is nec-

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essary that the buffer layer capacitance is as large as possible and that the leakage current density is as low as possible (Park and Ishiwara, 2003). It is important that the interfacial electrical properties do not degrade during the subsequent annealing needed for crystallizing the overlaid ferroelectric film. On the other hand, the interface used in a ferroelectric-gate FET may be more tolerant in the mobility degradation of inversion carries than that in an advanced CMOS-FET. The LAO film can be a buffer of a feroelectric-gate FET, since it has a relatively suitable permittivity (23–26) (Park and Ishiwara, 2003) and since the heat of formation values of both Al_2O_3 and La_2O_3 are so large that a transition layer such as SiO_2 is expected not to be formed. So far, LAO film can be fabricated on Si substrate by rf-magnetron sputtering, the chemical vapor deposition method and laser molecular-beam epitaxy (LMBE) technique (Xiang *et al.*, 2003). The sol-gel technique for preparing LAO film (Penanoya *et al.*, 2001), however, must be carried out with aluminum and lanthanum alkoxide system basing on methoxyethoxide complexes with 2-methoxythanol in an argon-filled or inter-atmosphere glove box (Shoup *et al.*, 1997). Our interest in LAO is to develop a novel sol-gel method to fabricate LAO thin film with corresponding inorganic in normal conditions. Reactivity of the lanthanum nitrate and aluminum nitrate with water is what drives the sol-gel process, but it must be properly controlled for forming a desired LAO sol without being precipitated during the hydrolysis. With glacial acetic acid as solvent, the metallic nitrates $La(NO_3)_3$ and $Al(NO_3)_3$ can be turned into the corresponding metallic acetates. After being refluxed for 20 min, $(CH_3CO)_2O$ separates the crystallized H_2O and nitrate completely from the solution. Under no water conditions, the $M(OAc)_n$ reacted with stoichiometrical acetylacetone (AcAc) and formed $M(OAc)_{n-x}(AcAc)_x$ complexes, which are hydrolyzed into $M(OH)_{n-x}$ $(AcAc)_x$ by addition of 10 ml 0.4% methyl cellulose (MCL). The hydroxylates, polymerizing and combining with MCL, formed a heteropolymeric $LaAlO_3$ sol. The gel LAO film obtained by spinning-coating had excellent uniformity and transparency. The annealing process of the gel $LaAlO_3$ film involved de-hydroxylation and condensation, nucleation, and growth of LAO crystals. DTA and TGA results of the LAO sol precursor indicated that the LAO sol lost ~93% of its weight at 123.2 °C by solvent evaporation; the 2% decrease in its weight at 299.98 °C to 394.53 °C was due to decomposition of the AcAc complexes, and organic templates, etc.; 500.31 °C might be the crystallizing point of the LAO gel.

X-RAY DIFFRACTION (XRD) OF THE LAO_3 FILM

XRD patterns of the LAO film after its being annealed from 550 °C to 850 °C are shown in Fig.1.

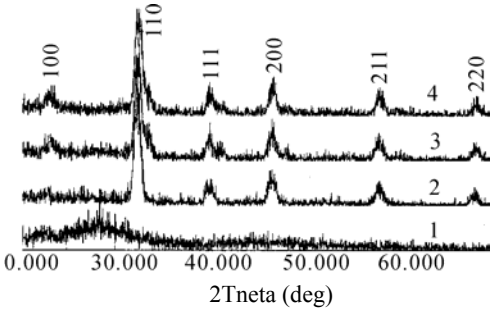
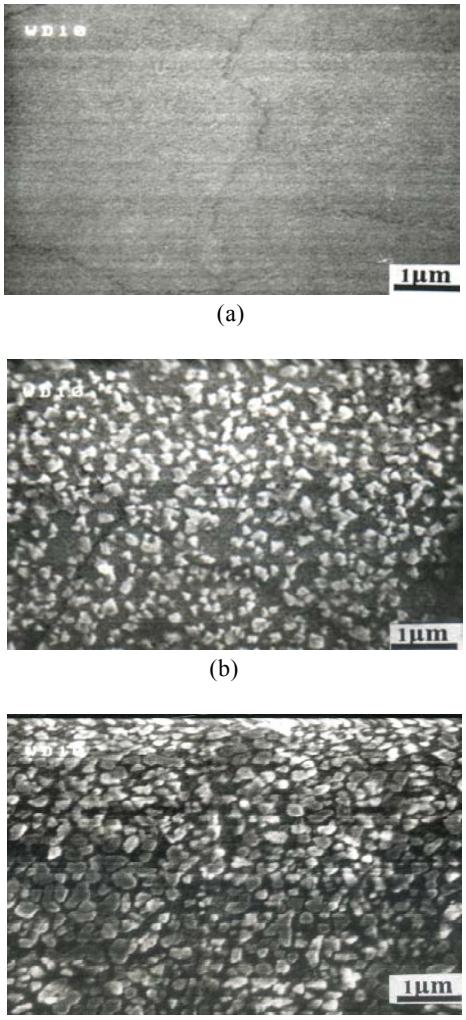


Fig.1 XRD patterns of the LAO film on Si(110) after being annealed (1: 550 °C/30 min; 2: 650 °C/30 min; 3: 750 °C/30 min; 4: 850 °C/30 min)

The $LaAlO_3$ film, after being annealed at 550 °C for 30 min, was completely amorphous and without any significant diffraction peaks; the film shows (110), (111), (200), (211) diffraction peaks, a well-cubic perovskite is formed after being annealed at 650 °C for 30 min, The well-cubic perovskite is stable until being annealed temperature 850 °C.

SEM AND PROPERTIES OF THE LAO FILM

Fig.2 shows SEM of the LAO film after its being annealed at 550 °C to 750 °C for 30 min respectively. The film appeared in amorphous state



(a)

(b)

(c)

Fig.2 SEM of the $LaAlO_3$ films after being annealed
(a) 550 °C, 30 min; (b) 650 °C, 30 min; (c) 750 °C, 30 min

after it was annealed at 550 °C, it was crystallized after it was annealed at 650 °C/30 min to a nanosize, and the average crystal grain size is grown about 0.15 μm after the film was annealed at 750 °C for 30 min. So the crystallizing process of the $LaAlO_3$ film occurred at low annealing temperature. The SEM micrograph of the LAO film on single crystal Si appeared to be continuous, flat, smooth and showed typical polycrystalline texture.

The refractive indexes of the LAO film, characterized by ellipsometer (Mizojiri Optical Co. Ltd DVA-36LD), were 1.942 to 2.007 after the film was annealed at 650 °C to 850 °C. The dielectric properties and dissipation factor were evaluated by HP4274A and 4275A automatic bridge (Hewlett Packard Inc., USA) with Au/$LaAlO_3$ film/Pt (MIM) structure, which was fabricated by depositing an Au electrode onto 200 μm diameter LAO film as top electrode; the bottom electrode Pt was deposited before the filming. The dielectric constants (ε_r') was about 23.98–26.18 and the dissipation factor ($\tan\delta$) was 2.3×10^{-4} to 2.4×10^{-4}.

CONCLUSIONS

LAO film with continuous, smooth and typical polycrystalline texture was prepared by LAO sol made by lanthanum nitrate hexahydrate and aluminum nitrate hexahydrate. The gel LAO film was crystallized into cubic perovskite structure after being annealed at 650–750 °C. The dielectric constant was 26.18–23.98, and the dissipation factor ($\tan\delta$) was 2.3×10^{-4} to 2.4×10^{-4}.

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