論文の内容の要旨

Hygroscopic Tolerance and Permittivity Enhancement of Phase-controlled La_2O_3 for High-k Gate Insulators

（高誘電率ゲート絶縁膜に向けたランタン酸化物薄膜の相を制御することによる耐吸湿性向上および高誘電率化の研究）

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The scaling of the silicon dioxide（SiO_2） layer thickness of the metal-oxide-semiconductor field effect transistor（MOSFET）gives rise to the unacceptable leakage current flowing through the metal-oxide-semiconductor structure. Therefore, high permittivity（*k*）materials are being considered to replace SiO_2 as the new MOSFET gate dielectric and insulator of（metal-insulator-metal）MIM capacitors. Lanthanum oxides（La_2O_3） are widely studied to substitute SiO_2 as high-*k* gate insulators due to its high permittivity and large band gap. However, it is well known that La_2O_3 is not stable in the air and very hygroscopic, forming hydroxide. To use it as a gate insulator, we have to enhance the hygroscopic tolerance of La_2O_3 film. Furthermore, there is a large scattering of the permittivity of La_2O_3 film, both very high permittivity（~28）and very low permittivity（~7）reported. In this study, firstly we investigated the hygroscopic and low permittivity phenomena of La_2O_3 films systematically. Then according to analyze the possible reasons for hygroscopic phenomena and low permittivity of La_2O_3 films, phase control of La_2O_3 film is proposed for enhancing the hygroscopic tolerance and permittivity. We demonstrated phase controlled La_2O_3 film with Y_2O_3 doping（$LaYO_x$ film）which not only shows strong hygroscopic tolerance, but also a high permittivity due to its good crystallinity hexagonal phase.

We found that the moisture absorption induces the formation of hexagonal La（OH）$_3$. Furthermore AFM results indicate that the moisture absorption also increases the surface roughness of La_2O_3 films due to the volume expansion after the moisture absorption because of the formation of low density hexagonal La（OH）$_3$. This should be another concern of La_2O_3 film’s application as a high-*k* gate insulator. Also the moisture absorption can induce the flat band voltage shift and hysteresis enlargement of C-V curve of La_2O_3 film.

The moisture absorption should be a very possible reason for the low permittivity La_2O_3 films reported because of the formation of La（OH）$_3$ with a lower permittivity after the moisture absorption. Furthermore, the permittivity of La_2O_3 without any moisture absorption is still a little low. This indicates that the low permittivity of La_2O_3 films can not be attributed to the moisture absorption phenomena totally.

The hygroscopic tolerance of La_2O_3 films were enhanced by Y_2O_3 doping due to the phase control, which suppresses the intrinsic reaction between La_2O_3 with H_2O. Furthermore, the larger lattice energy of Y_2O_3 is also an important factor to enhance the total lattice energy of La_2O_3. In the other hand, our experiment results indicate that the UV ozone post treatment can suppress the moisture absorption of La_2O_3 films to some degree. This suppression effect might come from the healing of oxygen vacancies in La_2O_3 films, since the oxygen ambient annealing also shows similar suppression effects.

We found that the permittivity of La_2O_3 film without moisture absorption is also a little low, only about 20. It means that the low permittivity of La_2O_3 can not be attributed to the moisture absorption totally. The poor crystallinity is also responsible for it. Therefore, we can enhance the permittivity of La_2O_3 by the crystallizing the film well. We prepared well crystallized $LaYO_x$ films with a high permittivity（~26）. The high permittivity is partly due to the higher permittivity hexagonal phase as the hexagonal phase shows a much larger permittivity than cubic phase for rare earth oxides（R_2O_3）. $LaYO_x$ film also shows very good electrical properties and a larger band.

Although $LaYO_x$ film shows a high permittivity and strong moisture-resistance to moisture, some researchers think that as gate dielectric amorphous film is with some merits due to many reasons. Therefore, here we also prepared amorphous $LaTaO_x$ films as high-*k* gate insulators. Furthermore, from the viewpoint of crystallization mechanism research, it will also be very interesting to investigate both easy crystallized and amorphous La-based oxides, which is also helpful for understanding other high-*k* oxide materials. Our results show that 35%Ta-$LaTaO_x$ film keeps amorphous even annealed at 1000 ºC. The high crystallization temperature of $LaTaO_x$ film is due to the large difference of valence state and ion size of La and Ta ions. Combining with reported results about La-based, we proposed a consistent explanation on the crystallization mechanism of La-based ternary oxides. At the same time, 35%Ta-$LaTaO_x$ film shows a permittivity as high as 30. We consider that the high permittivity is attributed to the high density of Ta_2O_5 which can induce a high permittivity although the $LaTaO_x$ film is amorphous. Larger band gaps of $LaTaO_x$ films than Ta_2O_5 were observed, which is due to the coupling effect between La 5*d* orbital and Ta 5*d* orbital through bonding to a common oxygen atom, the 5*d* anti-bonding state energy of Ta atom is enhanced and then the conduction band offset of Ta with Si is increased compared with that of Ta_2O_5. Therefore, the band gap of $LaTaO_x$ film is larger than that of Ta_2O_5.

In conclusion, the hygroscopic tolerance and permittivity of La_2O_3 films can be modulated with phase control due to Y_2O_3 doping. Y_2O_3 doped La_2O_3 films（$LaYO_x$）not only show a strong hygroscopic tolerance, but also a high permittivity which are very promising as high-*k* gate insulators for next generation CMOS devices.