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X-ray Photoelectron Spectroscopy Depth Profiling of La_2O_3/Si Thin Films Deposited by Reactive Magnetron Sputtering

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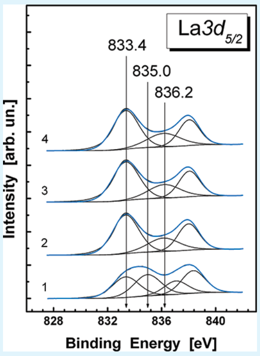
ABSTRACT: The La_2O_3/Si thin films have been deposited by reactive DC magnetron sputtering. Amorphous state of La_2O_3 layer has been shown by RHEED observation. Top surface chemistry of the *a*-La_2O_3 has been evaluated with layer-by-layer depth profiling by ion bombardment and XPS measurements. It was found by core level spectroscopy that the top surface of the *a*-La_2O_3 film consists of hydrocarbon admixture, lanthanum carbonate, and hydroxides that formed as a result of contact with air atmosphere. Thickness of this top surface modified layer is below 1 nm for a contact time of ∼1.5 h with air at normal conditions.



KEYWORDS: lanthanum trioxide, high-*k* dielectric, thin films, RHEED, XPS

1. INTRODUCTION

Lanthanum trioxide (La_2O_3) is one among the most promising high-*k* dielectric materials to replace SiO_2 and Si_3N_4 in advanced metal-oxide gate stack in semiconductor devices.[1−6] In thin film form the La_2O_3 oxide material can be found in several phases, namely, hexagonal (*h*-La_2O_3) with space group $P6_3/mmc$, cubic (*c*-La_2O_3) with space group $Ia\bar{3}$, amorphous (*a*-La_2O_3) or a mixture of the phases depending on the film deposition method and postdeposition heat treatment.[4,7−11] It is well-known that dielectric properties of La_2O_3 thin layers are strongly dependent on the phase composition, microstructure and doping. Highest dielectric permittivity $k \approx 27$ is reported for *h*-La_2O_3. Evidently surface chemical composition and structural properties of La_2O_3 films are of great importance for the compatibility of the dielectric layer into electronic device structure. Lanthanum trioxide is not inert with respect to atmosphere chemical agents and top surface hydration and carbonate formation are possible when La_2O_3 surface is in contact with air. These factors may be of great significance for interface chemistry and leakage current control in MOSFET gate layer stack. In this study, we report results of detailed observation of top surface chemistry of *a*-La_2O_3 layer after short time contact with air. For this purpose, the depth profiling of the *a*-La_2O_3 has been implemented by ion bombardment and X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL SECTION

The *a*-La_2O_3 thin films were deposited using reactive DC magnetron-sputtering of La-metal (99.9%) target in the reactive gas atmosphere containing oxygen and argon (O_2 + Ar). The deposition was made onto chemically well-cleaned Si(100) substrates. The deposition chamber was evacuated down to a pressure of 5×10^{-4} Pa prior to film-fabrication. The reactive gas mixture with oxygen partial pressure $O_2/(O_2 + Ar) = 24\%$ was introduced into the vacuum chamber and the pressure maintained during deposition was ∼0.1 Pa. The DC power during deposition was 255 W. The substrate temperature during deposition by $t = 1$ h was $T_s = 200$ °C providing amorphous state of La_2O_3 films. The amorphous state of deposited La_2O_3 films was confirmed by reflection high energy electron diffraction (RHEED) using the EFZ4 device (Carl Zeiss, Germany) under electron accelerating voltage of 50 kV. Only initial stages of polycrystalline structure formation can be revealed by the RHEED pattern shown in Figure 1. Film thickness was estimated as h = 82 nm with the help of ellipsometric measurements with using the model air − (homogeneous isotropic film) − (homogeneous isotropic infinite silicon substrate).

XPS measurements were performed on a SPECS's device equipped with an X-ray source with a twin Al/Ag anode, an ellipsoidal crystal X-ray monochromator FOCUS-500, a PHOIBOS 150 hemispherical electron energy analyzer, and an ion source IQE-11. The spectra were typically obtained using monochromatic Al $K\alpha$ radiation ($h\nu = 1486.74$ eV) and fixed analyzer pass energy of 20 eV under ultrahigh vacuum condition. The *a*-La_2O_3/Si sample was inserted into XPS chamber by 1.5 h after extraction from magnetron chamber. The layer-by-layer depth profiling of the film was carried out using an ion bombardment by Ar^+ ions with energy of 2.4 keV at an ion current density of 10 $\mu A/cm^2$. Ion bombardment was subsequently performed as a function of time, t = 2, 15, and 30 min. Depth profiling rate under these conditions was estimated as ∼0.5 nm/min in reference to SiO_2/Si film system. The

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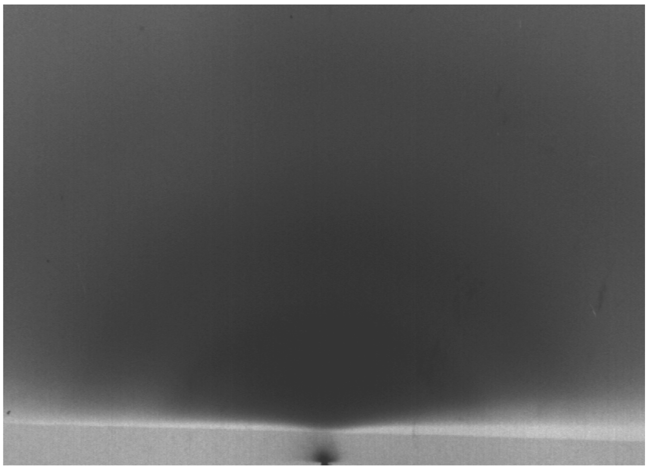

Figure 1. RHEED pattern recorded for *a*-La_2O_3 film.

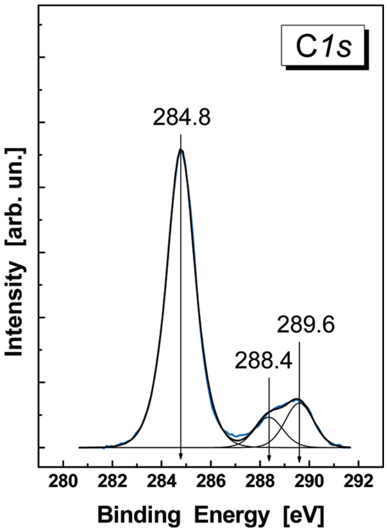

Figure 2. C1s core level spectrum for initial *a*-La_2O_3 surface.

Table 1. Surface Chemical Composition As a Function of Integrated Bombardment Time *t*

time, *t* (min)	[O]/[La]
0	3.7
2	1. 8
15	1.6
30	1.4

binding energy (BE) was calibrated using the C1s peak at 284.8 eV related to adventitious hydrocarbons for as-inserted surface and the $La3d_{5/2}$ peak at 833.35 eV for bombarded surface.

3. RESULTS AND DISCUSSION

In the survey XPS spectrum recorded for as-inserted *a*-La_2O_3 film surface, only the lines related to La, O, and C elements were observed. The C1s spectrum recorded for initial surface is shown in Figure 2. The intensive component at 284.8 eV is related to adsorbed hydrocarbons. Low intensity components with BE values of 288.4 and 289.6 eV are attributed to carboxyl and/or carbonate groups.[12−16] The intensity of C1s line becomes below detection level after first bombardment procedure during 2 min that indicates the hydrocarbon admixture localization into top surface layer. The [O]/[La] atomic ratios are shown in Table 1 as determined with using atomic sensitivity factors reported in

Table 2. Core Level Binding Energy As a Function of Integrated Bombardment Time *t*

	core level		
time, *t* (min)	C1s	$La3d_{5/2}$	O1s
0	284.8, 288.4, 289.6	833.4, 835.0	528.5, 531.2
2		833.4, 836.2	529.0, 531.4
15		833.4, 836.2	529.0, 531.4
30		833.4, 836.2	529.0, 531.4

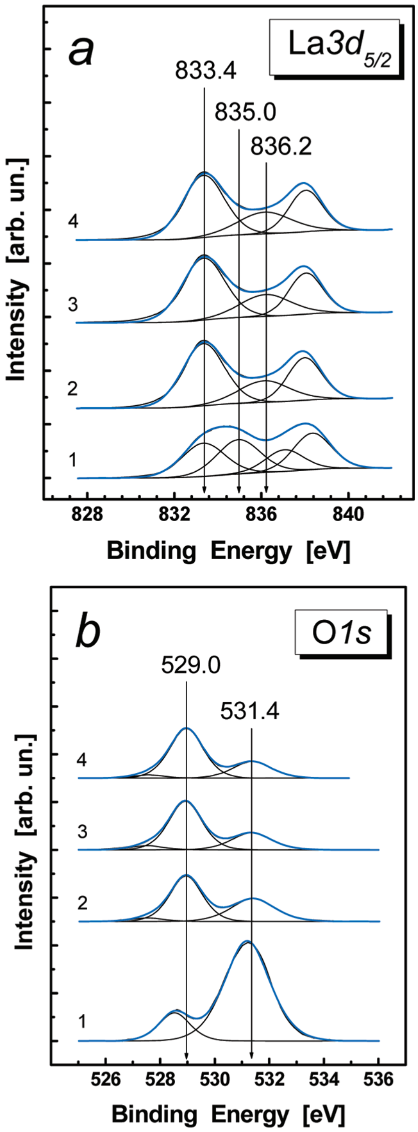

Figure 3. (a) $La3d_{5/2}$ and (b) O1s core level spectra of (1) initial surface and ion bombarded surface (2, 3, 4) for *t* = 2, 15, 30 min, respectively.

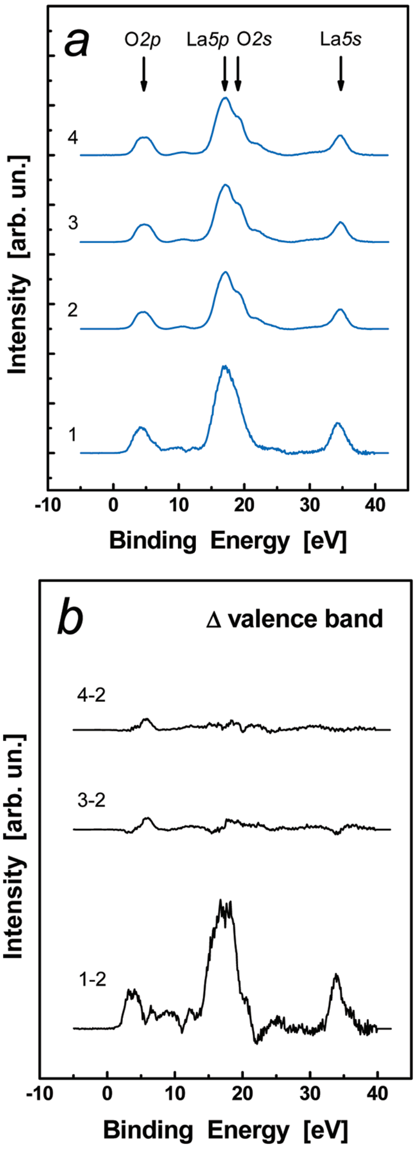

Figure 4. (a) Valence band and (b) difference spectra of (1) initial surface and ion bombarded surface (2, 3, 4) for t = 2, 15, 30 min, respectively. Intensity is normalized to that of related La3$d_{5/2}$ spectrum.

ref 17. For initial surface, the ratio [O]/[La] is evidently overestimated in reference to La_2O_3 stoichiometry that indicates the presence of CO_x and OH groups adsorbed on the surface. The presence of lanthanum hydrocarbonates cannot be excluded as well.

The core levels observed for bombarded a-La_2O_3 surface are shown in Table 2. The La3$d_{5/2}$ spectrum is shown in Figure 3(a) as recorded for initial and bombarded surface. The spectrum related to initial surface can be considered as a superposition of two doublets with BE values of 833.3/837.1 and 835.0/838.3 eV. Each doublet is formed by main line La3$d_{5/2}$ with lower BE value and "shake-up" satellite with few higher BE value and appeared because of hybridization of O2p and La4f orbitals.[18] In accordance with earlier XPS measurements the main La3$d_{5/2}$ line related to bulk La_2O_3 is positioned over the BE range of 833.2–834.0.[19−23] Higher BE values of 835.0–835.5 eV are typically observed for lanthanum carbonate $La_2(CO_3)_3$.[19−22] Close BE values of ~834.8 eV are also observed for lanthanum hydroxides LaOOH and $La(OH)_3$.[19,24] Respectively, the first doublet La3$d_{5/2}$ at 833.3/837.1 eV can be attributed to La_2O_3, whereas the second doublet La3$d_{5/2}$ at 835.0/838.3 eV seems to be related to lanthanum carbonates and hydrocarbonates. It should be pointed that in the second doublet La3$d_{5/2}$ at 835.0/838.3 eV, the relative intensity of "shake-up" satellite is higher than that of the main line. This effect was observed elsewhere earlier.[21]

After ion bombardment the components related to carbonates and hydroxides disappeared. However, in La3$d_{5/2}$ spectrum the wide component appeared with maximum at BE of 836.2 eV. Previously is was shown for many single-phase lanthanum-containing compounds that the La3$d_{5/2}$ spectrum is well-described by a set of basic line and "shake-up" satellite.[22,25−28] A doublet La3$d_{5/2}$ with peak maxima at 833.35/838.0 eV can be related to La_2O_3 oxide. Additive wide peak with maximum at BE of 836.1–836.2 eV seems be related to lanthanum suboxide LaO_x. Earlier, for example, the formation of suboxides HfO_x as a result of ion bombardment as probed by XPS was reported for HfO_2 films.[29,30] It is interesting that the "shake-up" satellite is absent in La3$d_{5/2}$ line of La metal and negative BE chemical shift is measured for initial stages of lanthanum oxidation.[16,31] As should be noted, in a result of ion bombardment the energy splitting between the main line and "shake-up" satellite of La3$d_{5/2}$ spectrum increases from 3.7 eV to 4.6–4.7 eV.

It was shown above that BE of "shake-up" satellite is noticeably dependent on local chemical environment of La^{3+} ions. For example, the energy splitting is 4.8 eV for pure La_2O_3 and as low as 3.7–3.8 eV for highly dispersed La_2O_3/Al_2O_3 systems.[23]

The O1s core level is shown in Figure 3b. Two lines at 528.5 and 531.2 eV with strongly different intensity are evaluated for the initial surface. The line at 528.5 eV is undoubtedly related to oxygen atoms in La_2O_3[20,24] and wide intensive band centered at ~531.2 eV seems to be related to oxygen atoms of hydroxyl and carbonate groups.[14−16] The ratio [O]/[C] defined by intensity of a component at ~531.2 eV of O1s band and integrated intensity of the components at 288.4 and 289.6 eV of C1s band yields a value of 4.7. This indicates that at the initial surface, besides carboxyl and carbonate groups, a significant quantity of hydroxyl groups is present. The intensity of the component at 531.4 eV is drastically decreased after first short time ion bombardment. In parallel the O1s component related to oxygen states of La_2O_3 is few shifted to 529.0 eV and remains to be independent of further ion bombardment time increase.

The spectra of valence band for initial and bombarded surfaces are shown in Figure 4. Mixed states band dominated by photoemission from O2p level is observed at 4.5 eV.[32] In the difference spectra obtained for bombarded surface a band appeared at ~5.7 eV that also may be attributed to O2p states on the basis of quantum chemical calculations for La-containing compounds.[32,33] An intensive complex band formed by La5p and O2s states is found at ~17 eV.[26,27,33] The sharp line at BE of ~35 eV is related to the La5s core level.

4. CONCLUSION

The XPS observation of surface properties of a-La_2O_3 films confirms swift chemical modification of this oxide by atmosphere agents. The reaction at normal conditions results in top surface formation of a mixture of lanthanum carbonate and hydroxides. Thickness of this modified layer is <1 nm for an air contact time ~1.5 h. This modified layer can be successfully removed by short time ion bombardment with Ar^+ with middle ion energy. The effect of suboxide LaO_x formation by ion bombardment is detected and, respectively, a procedure seems to be needed to restore the stoichiometric La_2O_3 composition by special treatment in oxygen or ozone atmosphere.

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