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Tuning the electrical resistivity of pulsed laser deposited $TiSiO_x$ thin films from highly insulating to conductive behaviors

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We report on the successful growth of amorphous $TiSiO_x$ thin films by means of pulsed-laser ablation of a TiO_2/SiO_2 composite target in a high-vacuum chamber. The room-temperature resistivity of the $TiSiO_x$ films is found to decrease by more than 6 orders of magnitude (i.e., from $\sim 2\times 10^4$ to 10^{-2} Ω cm) when their substrate deposition temperature (T_d) is increased from 20 to 600 °C. On the other hand, by subjecting these films to a post-deposition annealing at 600 °C in oxygen atmosphere, they become highly insulating with a resistivity level as high as 2×10^{10} Ω cm, regardless of the T_d value. The presence of conductive titanium silicide and titanium sub-oxide local phases in the as-deposited $TiSiO_x$ films, as revealed by photoelectron spectroscopy analyses, appears to be the cause of the observed tremendous change in the film resistivity. In particular, it is shown that the resistivity of the $TiSiO_x$ films is strongly correlated with their oxygen content. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1688999]

Materials belonging to the Ti–Si–O ternary system are well known to have attractive properties for microelectronic as well as photonic applications. For instance, the non-oxygenated phase of titanium and silicon [i.e., titanium silicide ($TiSi_2$)] has been widely used in advanced integrated circuit metallization for self-aligned processes technology.[1,2] For the latter purpose, $TiSi_2$ is one of the most attractive materials among the transition metal silicides because of its low resistivity and high thermal stability. On the other hand, the completely oxygenated phase of the Ti–Si–O system [i.e., titanium silicate ($TiSiO_4$)], is a dielectric material which can be seen as a homogeneous molecular mixture of the two highly resistive SiO_2 and TiO_2 oxides. In addition, mixing high-*k* metal oxides with a glassy material like SiO_2 is known to lead generally to the formation of amorphous metal silicate films.[3,4] Titanium silicate films were at first synthesized by means of sol-gel processing basically for planar optical applications such as antireflective coatings[5] and passive[6] or active waveguides.[7] Their growth by other methods including chemical vapor deposition,[8,9] sputtering,[10] and pulsed-laser deposition (PLD)[11] is rather recent. These studies have shown in particular that titanium silicate thin films exhibit not only a high dielectric constant (*k*) but also good breakdown strength.[8–11] This unusual combination of dielectric properties makes titanium silicate thin films highly attractive for the development of the next generation of submicron complementary metal–oxide–semiconductor devices. While the properties of the two extreme cases of the Ti–Si–O system, namely $TiSi_2$ and $TiSiO_4$, are quite well documented, those of partially oxygenated Ti–Si–O compounds (i.e., $TiSiO_x$) are still to be investigated.

In this letter we report on the successful growth of amorphous $TiSiO_x$ thin films by laser ablation from a TiO_2/SiO_2 composite target in high vacuum at various substrate deposition temperatures (T_d). The electrical as well as structural properties of these pulsed laser deposited (PLD) $TiSiO_x$ films have been investigated as a function of T_d. The effect of post-annealing the $TiSiO_x$ films in oxygen atmosphere on their room-temperature resistivity is also presented. The process thus developed permits the production of $TiSiO_x$ thin films with electrical resistivities ranging from highly insulating to fairly conductive.

The $TiSiO_x$ thin films were deposited from the pulsed laser ablation of an equi-atomic TiO_2/SiO_2 composite target (99.9% purity) using a KrF excimer laser ($\lambda = 248$ nm and 15 ns pulse duration) at a laser fluence of ~ 2 J/cm^2. The target–substrate distance was set at 6.5 cm. The $TiSiO_x$ thin films were deposited on conventionally cleaned Si (100), quartz and platinum-coated-Si substrates, under a chamber pressure of 10^{-5} Torr, at various T_d ranging from 20 to 600 °C. The thickness of the deposited films was determined to be of ~ 200 nm. Post-deposition annealings of the films were performed in a quartz tube furnace at a temperature of 600 °C in oxygen for 30 min. The resistivity of the deposited films was determined at room temperature either from four-point-probe measurements or from the low field Ohmic conduction region of $I-V$ curves of $Pt/TiSiO_x/Pt$ capacitor devices. The chemical bonding states and composition of the samples were systematically investigated by means of Fourier transform infrared (FTIR) and x-ray photoelectron spectroscopies (XPS). The XPS spectra were collected by using the ESCALAB 220I-XL spectrophotometer, equipped with an Al $K\alpha$ (1486.6 eV) monochromatic source, after a systematic *in situ* surface cleaning by means of 5 keV Ar^+ ions sputtering. The x-ray diffraction (XRD) analyses, at a glancing incident angle of 1°, have confirmed the amorphous char-

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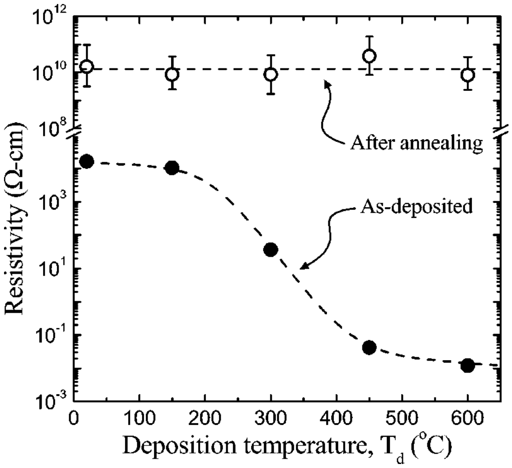

FIG. 1. Variation of the room-temperature resistivity of the as-deposited PLD $TiSiO_x$ thin films as a function of their substrate deposition temperature (closed circles). The resistivity of these films after their post-thermal annealing is also shown (open circles). Dashed lines are meant only as a guide.

acter of the PLD $TiSiO_x$ films regardless of their T_d and post-annealing treatment.

Figure 1 shows the room-temperature resistivity of the PLD $TiSiO_x$ films deposited at T_d ranging from 20 to 600 °C before and after annealing. For the as-deposited $TiSiO_x$ films, it is seen that the resistivity considerably diminishes when T_d is increased from 20 to 600 °C. Indeed, it changes by more than six orders of magnitude from 1.6×10^4 Ω cm (at $T_d=20$ °C) to 1.2×10^{-2} Ω cm (at $T_d=600$ °C). One should note that, while the resistivity of the $TiSiO_x$ films remains nearly constant between $T_d=20$ and 150 °C, the drastic resistivity drop is found to occur around $T_d=300$ °C. Moreover, all the resistivity values of the as-deposited $TiSiO_x$ films (more particularly for $T_d\geqslant450$ °C) are surprisingly low, given that the starting target material is composed of two highly resistive oxides (i.e., SiO_2 and TiO_2). Resistivity values as low as 1.2×10^{-2} Ω cm (obtained at $T_d=600$ °C) are much more characteristic of a conductor rather than an insulator. On the other hand, Fig. 1 shows that the electrical resistivity of the $TiSiO_x$ films is drastically affected by the post-deposition annealing treatment. Indeed, all the annealed films were found to exhibit nearly the same high resistivity level of 2×10^{10} Ω cm, regardless of their initial T_d. Thus, the annealing treatment transforms the $TiSiO_x$ thin films into a highly insulating material, showing that the electrical resistivity of such films can be changed by up to 12 orders of magnitude (for the films deposited at $T_d=600$ °C).

XPS and FTIR analyses have been performed on the $TiSiO_x$ films in an attempt to pinpoint the microstructural changes that would explain such a large resistivity variation as a function of T_d and/or post-annealing treatment. Figure 2(a) shows the Si_{2p}, Ti_{2p}, and O_{1s} core level XPS spectra of the PLD $TiSiO_x$ films as a function of their T_d and after their annealing. The O_{1s} spectra of both as-deposited and annealed $TiSiO_x$ films show only a single peak of which position (i.e., 531.3 eV) is found to occur between the binding energy values of O_{1s} into SiO_2 and TiO_2 materials (i.e., 532.6 and 529.7 eV, respectively).[12] This indicates that the TiO_2/SiO_2 constituent phases of the target were molecularly mixed during the film growth process giving rise to the formation of

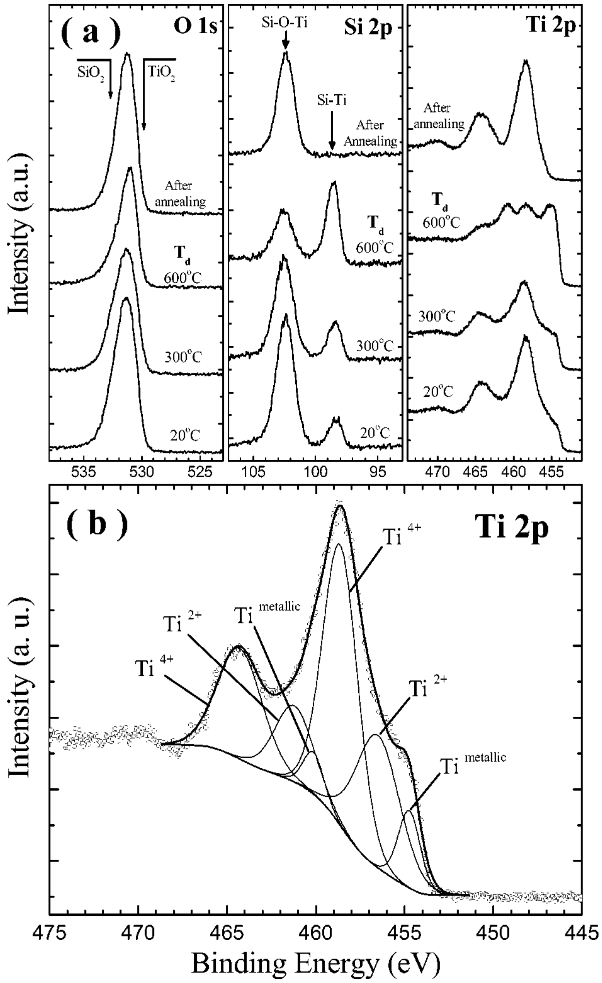

FIG. 2. (a) High resolution XPS spectra of O_{1s}, Si_{2p}, and Ti_{2p} core levels of the PLD $TiSiO_x$ thin films as a function of their deposition temperature. The corresponding XPS spectra of the annealed films are also included; (b) typical deconvolution of the Ti 2*p* photoelectron spectra (the spectrum shown here is for the films grown at $T_d=300$ °C).

Ti–O–Si type of bondings (instead of Ti–O and Si–O segregated environments), which characterize the Ti–Si–O silicate phase. The formation of the silicate phase is also confirmed by the FTIR spectra (not presented here) of the PLD $TiSiO_x$ films that have systematically shown the presence of the absorption band corresponding to the Si–O–Ti stretching vibrations centered at a wave number of 940 cm^{-1}.[13] On the other hand, the Si_{2p} and Ti_{2p} XPS peaks were found to consist of more than one component, suggesting thereby the presence of different local environments of either Si or Ti atoms in the films. Indeed, the middle panel of Fig. 2(a) shows two distinct peaks of Si_{2p} at binding energies of 102.5 and at 98.6 eV. While the peak at 102.5 eV is characteristic of the titanium silicate phase, the peak at 98.6 eV indicates the presence of Si–Ti metallic bonds in the films, as those typically encountered in the titanium silicide phase.[2,12,14] One should note that, as T_d is increased from 20 to 600 °C, the "silicide" part of the Si_{2p} XPS spectra remarkably increases to the detriment of the silicate part (i.e., Si–O–Ti bondings). (The ratio of the peak area of the "silicide" to the silicate components increases from 0.1 to 1.0 when T_d is raised from 20 to 600 °C.) Finally, after annealing, the Si_{2p} peak is clearly seen to consist of *only* the fully oxidized

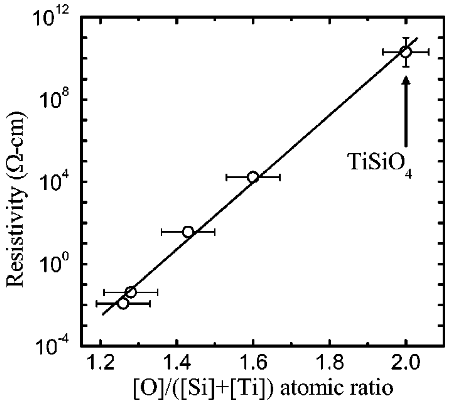

FIG. 3. Cross plot of the room-temperature resistivity of PLD $TiSiO_x$ films as a function of their oxygen content, as determined from XPS measurements.

Si–O–Ti silicate component [the Si–Ti silicide peak has completely disappeared; see Fig. 2(a)]. This is very consistent with the highly insulating behavior of the films after their annealing under O_2. The analysis of the Ti_{2p} peak [Fig. 2(a)] gives some further insights into the chemical bondings of the $TiSiO_x$ films. Indeed, the Ti_{2p} peak deconvolution [Fig. 2(b)] not only confirms the presence of the silicate (Ti^{4+}) and silicide (Ti^{metallic}) bonding states into the films but also reveals the presence of Ti^{2+} type of local environments (as those forming titanium sub-oxides).[14] Both the ''sub-oxide'' (i.e., Ti^{2+}) and ''silicide'' components of the Ti_{2p} peaks were found to increase with T_d to the detriment of the silicate one, which is the only phase present after annealing [see Fig. 2(a)—top of the right panel].

The presence of silicide-like and Ti-sub-oxide-like environments in the films suggests a lack of oxygen atoms to form the completely oxidized $TiSiO_4$ phase. Indeed, the composition of the films, as determined by XPS, confirms that the [O]/([Si]+[Ti]) atomic ratio is of $\sim$1.6 at $T_d = 20\,°\mathrm{C}$ and continuously diminishes with the increase of T_d to reach 1.2 for the films deposited at 600 °C. After annealing, this atomic ratio is found to recover a value of $\sim$2, which corresponds to the stoichiometry of the $TiSiO_4$ silicate phase. On the other hand, the cross plot of Fig. 3 shows that the resistivity of the $TiSiO_x$ films varies in a strikingly exponential manner with their oxygen content, over a resistivity range as wide as 12 decades. The straightness of this curve over such a wide range is quite remarkable and would lead one to suppose that the resistivity of these PLD $TiSiO_x$ films obeys some barrier-controlled conduction mechanisms.[15]

The observed variation of oxygen content of the $TiSiO_x$ films as their T_d is increased is thought to be a consequence of thermally induced oxygen desorption from the film surface during its growth. (Oxygen desorption has been reported to occur at the surface of TiO_2 in a high-vacuum environment at a temperature of about 300 °C,[16] which coincides with the T_d at which a sudden drop of resistivity is observed in Fig. 1.) Oxygen depletion that occurs in the films leads to the formation of silicide and Ti–sub-oxide bondings of which density and/or extent is found to increase with T_d, as revealed by XPS. The increasing presence of silicide and Ti–sub-oxide phases (which are known to be conductive with resistivities of 75 $\mu\Omega$ cm for $TiSi_2$,[1] and 10^{-2} and 2×10^{-4} Ω cm for Ti_2O_3 and TiO, respectively)[14,17] is thought to be the basic cause of the lowering of the resistivity of the $TiSiO_x$ films as their T_d is raised. After annealing, a complete oxidation is achieved and insulating $TiSiO_4$ films are obtained.

In conclusion, the pulsed laser deposition technique has been successfully used to deposit $TiSiO_x$ thin films with electrical resistivities that can be controlled over the (10^4-10^{-2}) Ω cm range by choosing a T_d in the (20–600) °C range. This large variation of the $TiSiO_x$ films resistivity is believed to be due to thermally induced oxygen depletion during the film growth which, in turn, leads to the formation of silicide and Ti–sub-oxide bondings. Postannealing of the $TiSiO_x$ films under O_2 is shown to result in the formation of completely oxidized, and consequently highly insulating $TiSiO_4$ phase. These results clearly demonstrate the crucial role played by oxygen incorporation into the $TiSiO_x$ films in determining their electrical resistivity. In particular, it has been shown that the resistivity of the films, over a range as wide as 12 orders of magnitude, is strongly correlated to their oxygen content.

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