

## Single crystalline highly epitaxial Pt thin films on (001) SrTiO<sub>3</sub>

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(001) oriented Pt thin films with excellent single crystal quality were epitaxially grown on (001) SrTiO<sub>3</sub>. The interface relationship was determined and shown to be (001)<sub>Pt</sub>∥(001)<sub>STO</sub> and [100]<sub>Pt</sub>∥[100]<sub>STO</sub>. Two unexpected “transitions” were found at 138 and 34 K in the evolution of resistivity with temperature as the samples were heated up, which can probably be attributed to phase transitions of the single crystalline SrTiO<sub>3</sub>. The fact that epitaxial (001) Pt film growth is observed under oxygen plasma is believed to be a result of oxygen ashing of S-containing impurities in the Pt target. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890844]

Micro- and nanoelectronic technologies have rapidly been advanced recently against its benchmark both in terms of capabilities and critical dimensions.<sup>1</sup> Many integrated electronic circuits require a stable bottom electrode in their sandwiched multilayered structures. Noble metal platinum (Pt), with its low resistivity, high thermal stability, and high stability under an oxygen environment at high temperature, is commonly considered as a good candidate for the bottom electrode material in various microelectronic devices.<sup>2–4</sup> Especially, Pt has a face-center-cubic structure with a lattice parameter of 0.3923 nm, which has very good lattice matching to a number of ferroelectric materials, such as (Ba,Sr)TiO<sub>3</sub>,<sup>5,6</sup> Ba(Ti,Zr)O<sub>3</sub>,<sup>7</sup> and lead zirconium titanate.<sup>8</sup> Although ultrathin Pt films can be grown on oxide surfaces such as (0001) Al<sub>2</sub>O<sub>3</sub> and (0001) ZnO,<sup>9,10</sup> earlier studies have indicated that Pt thin films cannot be epitaxially grown on the (001) SrTiO<sub>3</sub> surface due to the three dimensional island growth or the Volmer–Weber growth resulting from the formation of a Schottky barrier of ~0.4 eV high at the interface of Pt–SrTiO<sub>3</sub>.<sup>11,12</sup> Our recent experiments indicated that Pt thin films on (001) SrTiO<sub>3</sub> are always (001) and (111) coexistent, suggesting that the as-grown Pt films are polycrystalline. However, we found that Pt film can be of (001) texture when introducing a small amount of oxygen gas into the sputtering gas. In this letter, we report such Pt film epitaxial growth on (001) SrTiO<sub>3</sub> substrate with good electrical conductivity.

Pt thin films were deposited on (001) SrTiO<sub>3</sub> by both dc- and rf-magnetron sputterings using an extra high purity (99.999%) Pt target with its dimensions of 1 in. diameter and 0.125 in. thickness. It was presputtered in pure Ar with a pressure of 20 mTorr and 35 W for 30 min. Pt films were then deposited at various oxygen to Ar ratio of 0%–30% at substrate temperatures of 650–850 °C. The optimal epitaxial growth condition was found to be at 20 mTorr in an

oxygen-Ar ratio of 10%–20% and at 750 to 800 °C. The average growth rate is about ~1.0 nm/min and the typical film thickness is about 150 nm. To understand the quality of the as-grown Pt films, x-ray diffraction, scanning tunneling microscopy, and transport property measurement were employed to analyze the growth behavior, crystallinity, and electrical conductivity.

Figure 1 shows a  $\theta$ - $2\theta$  scan from x-ray diffraction of a Pt thin film grown on (001) SrTiO<sub>3</sub> at 780 °C and process pressure of 20 mTorr with the oxygen blend of 0% (black) and 10% (red plot). As seen in Fig. 1, both (001) and (111) peaks were clearly seen in the diffraction pattern (black) for the Pt thin film grown in pure argon sputtering, although the (001) peaks were dominant. This indicates that the as-grown Pt thin film on the (001) SrTiO<sub>3</sub> surface was neither epitaxial growth nor single crystalline. However, the (111) peak is absent from the diffraction pattern when the Pt thin film is grown in an oxygen-doped argon sputtering, as seen in Fig. 1 (red plot). In this case, only (001) peaks are observed in the

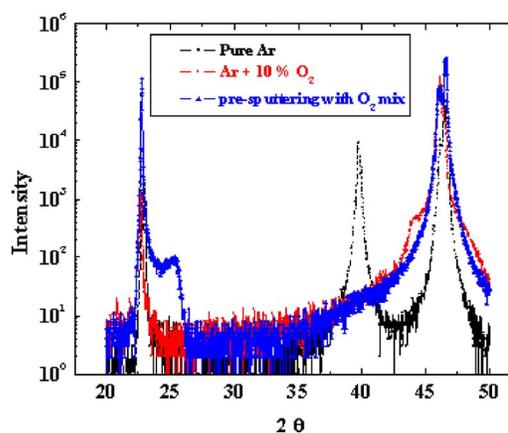


FIG. 1. (Color online) X-ray diffraction showing the growth nature of the as-grown films under different oxygen ratios (black plot: no oxygen, red plot: 10% oxygen, and blue plot: presputtered with 10% oxygen and grown with no oxygen).

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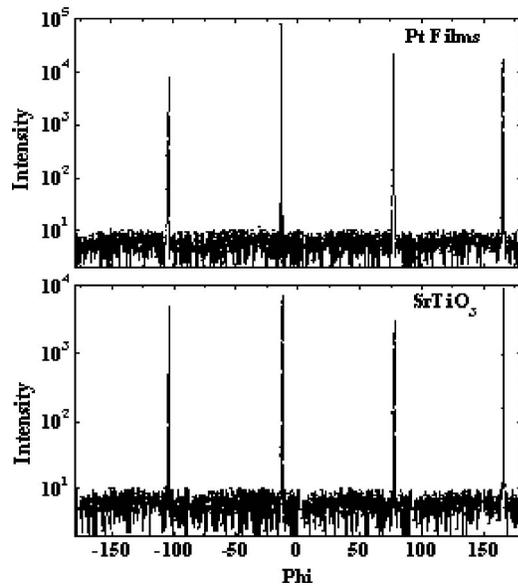


FIG. 2. X-ray phi scan showing the crystal quality of the as-grown Pt film on (001) SrTiO<sub>3</sub>, (up) Pt film and (down) SrTiO<sub>3</sub> substrate.

diffraction pattern, indicating that the as-grown Pt thin films are *c*-axis oriented. A rocking curve measurement of the (002) reflection showed that the full width at half maximum (FWHM) was about 0.4°. This observation suggests that the as-grown Pt thin film is basically single crystalline. It should be pointed out here that the broadened shoulder on the (004) reflection from this Pt films probably results from the strain effect in the Pt films due to the high degree of epitaxy on the (001) SrTiO<sub>3</sub>.

To fully understand the crystallinity, a phi scan of x-ray diffraction was taken to investigate the growth nature of Pt thin films on (001) SrTiO<sub>3</sub>. Figure 2 shows the reflection pattern from {220} planes for a Pt thin film grown in the 10% oxygen +90% argon mixture, revealing that the Pt film is not only a highly oriented crystalline but also is well aligned in the planes of substrate surfaces. The four extremely sharp peaks with equal degrees of separation for the {220} reflections suggest that the as-grown Pt thin film has excellent single crystal quality. The FWHM value for the Pt peaks is only 0.2°, which is consistent with the previous rocking curve measurement. From the reflection peak positions of the Pt corresponding to the peak positions in SrTiO<sub>3</sub> substrate, the in-plane relationship between the Pt thin film and the SrTiO<sub>3</sub> substrate was determined to be (001)<sub>Pt</sub>∥(001)<sub>STO</sub> and [100]<sub>Pt</sub>∥[100]<sub>STO</sub>. In other words, the unit cell axes of the Pt thin film are parallel to the unit cell axes of the SrTiO<sub>3</sub> substrate. This interfacial relationship gives rise to a lattice misfit of only about 0.46%. The strain energy from the lattice misfit can be released by forming misfit dislocations at the interface between the film and the substrate.

The results seem to somewhat conflict with the previous observations that Pt does not grow epitaxially on the (001) SrTiO<sub>3</sub> surface. Chung Yarmarkin and Teslenko<sup>8</sup> and Roberts and Gorte<sup>9</sup> studied the growth behavior of Pt on (001) SrTiO<sub>3</sub> surfaces and concluded that a potential barrier of ~0.4 eV was formed at the Pt–SrTiO<sub>3</sub> interface. This was attributed to a surface charge transfer from the SrTiO<sub>3</sub> to the Pt atoms during the growth of Pt thin films on the (001) SrTiO<sub>3</sub> surface. That is, an electron must penetrate a potential barrier of 0.4 eV in order to be transported from SrTiO<sub>3</sub>

to a Pt atom due to the strong interaction between the Pt and Ti atoms. Therefore, it is very difficult for the thin film process to occur at the film deposition temperature without an external potential. Wrighton *et al.*<sup>13,14</sup> reported that hydrogen flattens the Schottky potential at the Pt–SrTiO<sub>3</sub> interface so that electrons flow from the SrTiO<sub>3</sub> to the Pt surface. Thus, ultrathin Pt thin films were epitaxially grown on the (001) SrTiO<sub>3</sub> surface with the assistance of hydrogen.

The fact that *c*-axis oriented highly epitaxial Pt thin films on (001) SrTiO<sub>3</sub> were grown in an oxygen-argon mixture could be the result that the oxygen flattens the Schottky potential. However, it is more likely that oxygen reacts with the Pt target and removes some impurity atoms from the target during the Pt sputtering. The impurity removed from the target during oxygen-argon sputtering is very likely to be sulfur because metallurgical process usually uses sulfur as a catalyst to purify Pt. Ahmad and Tsong<sup>15</sup> studied impurity segregation from the Pt–Rh alloys using atom-probe field ion microscopy (AP-FIM) and concluded that the segregated sulfur impurity formed the top layer on the surface of the Pt–Rh alloy. Later, Chen and Tsong<sup>16</sup> also found the sulfur segregated from a high purity Pt surface (99.999%) at 700 °C in their AP-FIM studies. To verify that impurity effect, 10%–20% of oxygen was introduced into the system during the presputtering for 30 min and then the oxygen-argon mixed gases were pumped out from the deposition system (lower than  $1 \times 10^{-6}$  Torr) before the Pt films were grown in a pure Ar gas environment. The x-ray diffraction reveals that only (00l) peaks appeared in the pattern, as seen in Fig. 1 (blue plot), indicating that the Pt film is *c*-axis oriented, which suggests that the epitaxial Pt film does not depend on the existence of oxygen but on the target quality. If oxygen plays a similar role as what the hydrogen does to flatten the SrTiO<sub>3</sub> surface energy level, the as-grown Pt on (001) SrTiO<sub>3</sub> with oxygen presputtering should be polycrystalline. Therefore, it is reasonable to assume that sulfur impurities exist in the target. Once on the SrTiO<sub>3</sub> surface, the sulfur atoms might become absorbed and form nucleation seeds for the Pt thin films, resulting in (111) oriented Pt thin film growth. The introduction of oxygen or hydrogen plasma results in a chemical reaction between the sulfur atoms and oxygen or hydrogen gases to form volatile SO<sub>2</sub> or H<sub>2</sub>S vapors during the sputtering process. Such vapors are pumped out of the vacuum system during the film growth and do not affect the Pt film growth or the surface states of the SrTiO<sub>3</sub> surface. Although energy-dispersive x-ray (EDX) did not detect any signals of sulfur in the pure Ar-sputtered film, it is expected that sulfur is in such low concentration that it is below the detection limit of EDX. On the other hand, positive Ar ion bombardment from the bias on the sample surface could limit the Pt film nucleation density and increase the atomic mobility of the incoming atoms; these highly mobile atoms, when encountered with the highly oriented growing grains, could further strengthen the observed textured Pt film growth.

Figure 3 shows a plot of electrical resistivity versus temperature for the *c*-oriented highly epitaxial Pt films together with that from the bulk Pt single crystal.<sup>17</sup> The electrical resistivity linearly increases with the increase of the temperature, similar to the single crystal behavior. However, three anomalies were found in the evolution of resistivity with temperatures between the films and the bulk: (1) two distinct “transitions” occurred at  $T=34$  and 138 K were found in the

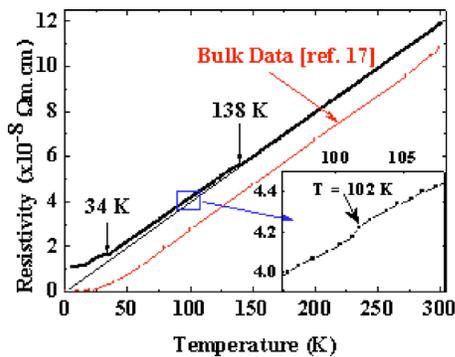


FIG. 3. (Color online) Temperature dependence of electrical resistivity for the *c*-oriented highly epitaxial Pt thin films on (001) SrTiO<sub>3</sub>. Two transitions were found at temperatures of 34 and 138 K. The inset shows that a slight resistivity shift occurs at 102 K, which corresponds to the phase transition of SrTiO<sub>3</sub>.

Pt film, whereas the bulk Pt resistivity does not exhibit similar behavior, (2) a more subtle change at 102 K (as seen in the inset), though with opposite polarity as those identified in (1), and (3) resistivity of Pt film is generally higher at a given temperature compared with the bulk values. Since resistivity is derived from surface resistivity measurement, inconsistencies in thickness measurement may contribute to the observed discrepancies. However, the nature of the transitions seems to be very interesting; some of them are probably induced by the substrate phase transitions. There are two known phase transitions in single crystalline SrTiO<sub>3</sub> which occur at 33 and 104 K.<sup>18</sup> The transitions at 34 and 102 K are close to those temperatures within the set measurement resolution and are likely a result of those substrate phase transitions. The substrate microstructural-change-induced film stress can easily affect electron scattering and resistivity in the highly epitaxial films. However, it is not fully understood yet on the mechanisms of the film resistance change by a quantum transition<sup>19</sup> at the lower temperature of 33 K in the SrTiO<sub>3</sub> substrate. Notice that the polarity of the transition at 34 K is opposite from that of 102 K, probably indicative of a difference in operating mechanisms, but is the same as that at 138 K. There has not been a creditable explanation on the source at 138 K. Detailed investigations about these unusual phenomena are on the way and will be reported later.

In summary, we have epitaxially grown a *c*-axis oriented single crystalline Pt films on (001) SrTiO<sub>3</sub> by using dc/rf

sputtering with an oxygen-argon mixture. Microstructure studies suggest that the epitaxial Pt film has excellent single crystallinity with good electrical conductivity, similar to the single crystal Pt bulk materials. The in-plane relationship of the as-grown Pt thin film on (001) SrTiO<sub>3</sub> was determined to be (001)<sub>Pt</sub>∥(001)<sub>STO</sub> and [100]<sub>Pt</sub>∥[100]<sub>STO</sub>. Strong strain effect from the substrate phase transitions was observed in the transport property measurements.

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