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Achievement of zero temperature coefficient of resistance with RuO_x thin film resistors

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The temperature coefficient of resistance (TCR) for an as-deposited $RuO_{2.2}$ thin film resistor changes from −131.6 to 1007.95 ppm/°C after the annealing at 600 °C for 30 min. Typically, a near zero TCR about 0 ± 0.12 ppm/°C can be obtained after annealing at 300 °C for 30 min in an Ar ambient. The changes of TCR from negative to positive is attributed to the grain growth of RuO_x films from fine grain (30–40 Å) to a larger one (500–800 Å) during the annealing process. Rutherford backscattering spectroscopy and *in situ* x-ray photoemission spectroscopy show that the ratio of O/Ru in the RuO_x film decreases from 2.2 to 2.0, due to the out diffusion of oxygen during the annealing process, which is independent of the changes in TCR. © *1997 American Institute of Physics.* [S0003-6951(97)01302-8]

In the past several years, ruthenium oxide (RuO_x) has become one of the very attractive metallization materials used for the dynamic random access memory (DRAM) because RuO_x exhibits an excellent thermal stability as a diffusion barrier between SiO_2 and Al overlayer during post annealing processes.[1] It is also used for the stable bottom electrode of ferroelectric capacitors in the non-volatile RAM where ferroelectric is used as dielectrics.[2,3] On the other hand, the RuO_x thin film has been suggested for applications in hybrid microcircuits and precise measurement instrumentation as a thin film resistor because of its relatively lower temperature coefficient of resistance (TCR) than the conventional ceramic resistors.[4] A near zero TCR (ppm/°C) is a critical property of thin film resistors used for highly accurate electronic measurement instruments.[5] However, most of the previous results on RuO_x thick and thin film resistors have concentrated on the film properties and TCR characteristics. Although it has been known that the TCR is a function of the substrate temperature and oxygen pressure during the sputtering processes of RuO_x thin films,[4,6,7] the influence of both the O/Ru ratio and the grain size on TCR is still not quantitatively investigated. In this work, we have tried to investigate qualitatively and quantitatively the dependence of TCR on the ratio of O/Ru and the grain size of RuO_x thin films as-deposited and annealed at temperatures of 200–600 °C.

p-type (100) Si wafers 4 in. in diameter were cleaned and SiO_2 with a thickness of 500 nm was thermally grown on these wafers. The RuO_x thin films were reactively sputtered on SiO_2/Si layers using a dc magnetron sputtering system. The target was a Ru pellet with a purity of 99.99% and 10 cm in diameter. The substrate temperature was maintained at 40 °C during the sputtering process. The flow rates of Ar and O_2 gases were seperately controlled with mass flow controllers and introduced into the sputtering chamber. The total working gas (O_2+Ar) pressure was kept at a constant level of 10 mTorr. More details about deposition procedures and properties of the RuO_x thin films were already reported in a previous work.[8] Several different patterns on a shadow mask allow the RuO_x thin film resistors to be patterned directly during the sputtering process. The resistances of these RuO_x film resistors varied from 1 to 5 kΩ depending on the length of the patterns. All of the RuO_x thin films had a thickness of 100 nm and the width of the resistor was fixed at 200 μm. The ratio of O/Ru in the RuO_x thin films was controlled with the flow ratios of $O_2/(O_2+Ar)$ from 10% to 50% and was determined by Rutherford backscattering spectrometry (RBS). The resistivity of RuO_x was varied from 155 to 260 μΩ cm corresponding to the ratio of O/Ru. The TCR of RuO_x thin film resistors was determined with the change in resistance relative to the resistance measured at room temperature, which is normalized by the temperature change from 25 to 180 °C. During the TCR measurement the RuO_x thin film resistors were kept on a heating stage in an isolated vacuum oven. In order to find a relationship between the TCR and the O/Ru ratio of the RuO_x thin film resistors, the resistors were annealed at a temperature range of 200–600 °C for 30 min in an Ar ambient. Also, some samples were annealed at 300, 500 and 600 °C for 30 min and introduced into the detection chamber without exposing the annealed samples in the atmosphere ambient for an *in situ* x-ray photoemission spectroscopy (XPS) measurement. As a result, the XPS spectra of O_{1s} and Ru_{3d} were quantitatively

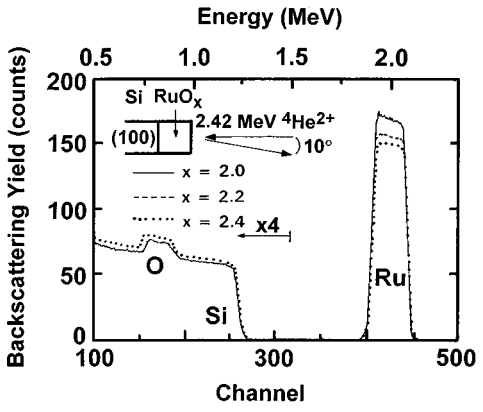

FIG. 1. RBS spectra for RuO_x thin films deposited with $O_2/(O_2+Ar)$ flow ratios of 10%, 30%, and 50%.

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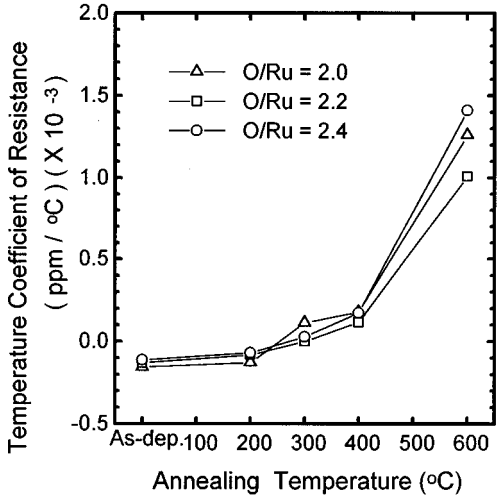

FIG. 2. TCR of as-deposited and annealed RuO_x thin films.

and qualitatively traced with this *in situ* XPS. The grain sizes of the RuO_x thin film were also investigated with transmission electron microscopy (TEM) after the annealing processes.

Figure 1 shows the RBS spectra for RuO_x thin films deposited with various $O_2/(O_2+Ar)$ flow ratios of 10 (solid line in Fig. 1), 30 (dashed line) and 50% (dotted line). Corresponding to these % of $O_2/(O_2+Ar)$, the ratio of O/Ru, x, is determined with the backscattering yields from O and Ru target atoms as follows; x increases from 2.0 to 2.2 and 2.4 while the flow ratio of $O_2/(O_2+Ar)$ varies from 10 to 30% and 50%, respectively. Figure 2 shows the TCR of RuO_x thin film resistors with three different O/Ru ratios. The TCR of as-deposited RuO_x resistors seems to be insensitive to changes in x from 2.0 to 2.4. The TCR remains at the same order of magnitude, although a lower oxygen content results in a slightly more negative TCR: i.e., the TCR for the $RuO_{2.0}$ film resistor is -158.3 ppm/°C, compared to -129.4 ppm/°C for $RuO_{2.4}$. Figure 2 also summarizes the dependence of the TCR on annealing temperatures for the thin film resistors with three different O/Ru ratios. As the annealing temperature increases from 200 to 600 °C the TCR changes sign from negative to positive. A TCR value of 0 ± 0.12 ppm/°C can be realized at a critical annealing temperature of 250–300 °C depending on the O/Ru ratios: i.e., a near zero TCR can be obtained with the $RuO_{2.2}$ thin film resistor after annealing at 300 °C for 30 min in an Ar ambient, whereas the other samples (x is greater or smaller than 2.2) have TCRs as low as 0 ± 3 ppm/°C after annealing at 250 °C for 30 min. Some reports mentioned that the TCR of RuO_x thin film resistors may be influenced by oxygen content.[7] How-

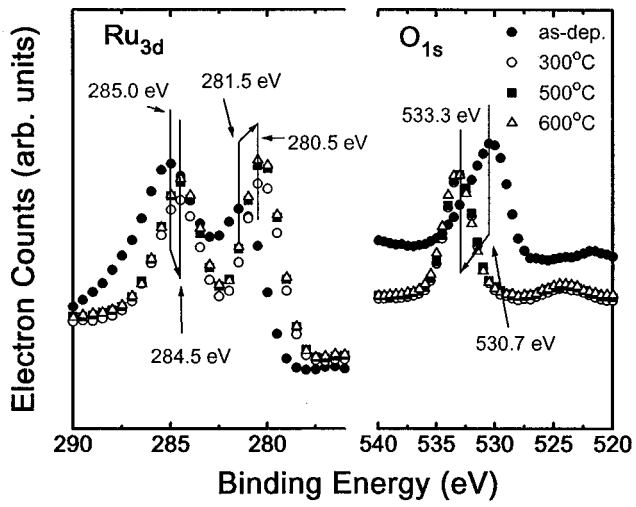

FIG. 3. Variation of XPS spectra for O_{1s} and Ru_{3d} corresponding to the as-deposited state and the annealed states at 300, 500, and 600 °C, respectively, for the $RuO_{2.2}$ stoichiometry films.

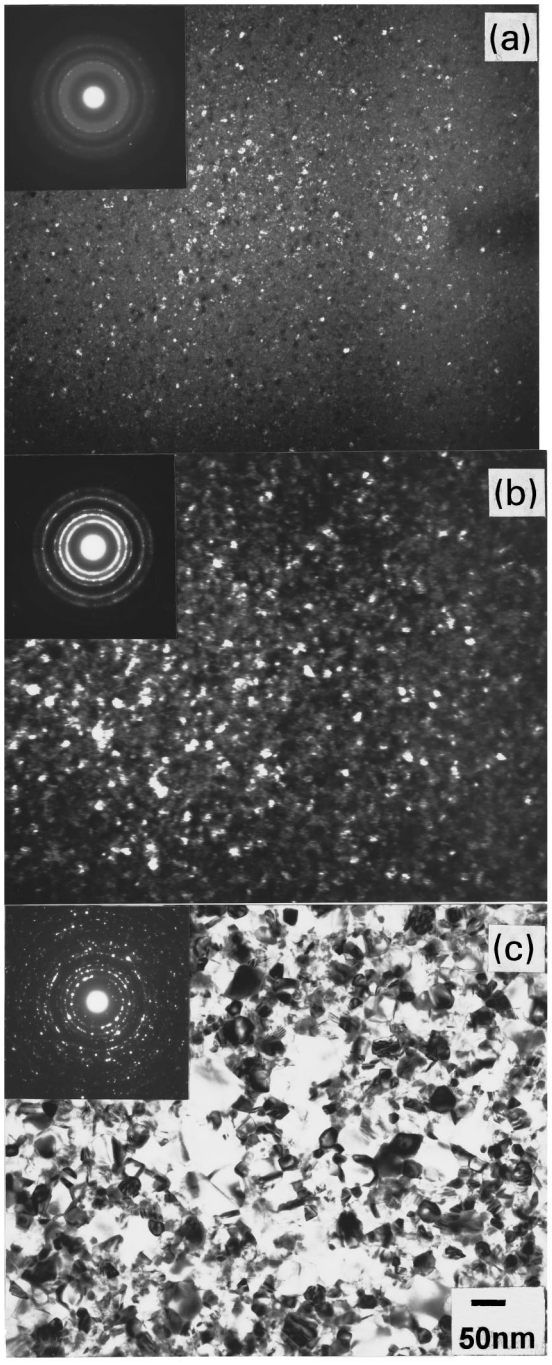

FIG. 4. TEM micrographs and SAD patterns for (a) as-deposited $RuO_{2.2}$ thin film, and $RuO_{2.2}$ thin film annealed at (b) 300 and (c) 600 °C, respectively.

ever, our results obviously indicate that the TCR of RuO_x thin film resistors is nearly independent of the O/Ru ratio. To see the dependence of TCR on the O/Ru ratio in the RuO_x films, *in situ* XPS was used to investigate the chemical binding energies and emission intensities of O and Ru photoelectrons during the annealing processes. Figure 3 shows the variation of XPS spectra for O_{1s} and Ru_{3d} corresponding to the as-deposited and annealed $RuO_{2.2}$ films at temperatures of 300, 500, and 600 °C. The spin orbit coupling of the Ru_{3d} subshell has two states of j values, 3/2 and 5/2, which are observed around 285 and 281.5 eV, respectively and the spectra of O_{1s} is found at 530.7 eV for the as-deposited the $RuO_{2.2}$ thin film. When the $RuO_{2.2}$ film is annealed at a temperature above 300 °C the $Ru_{3d3/2}$ and $Ru_{3d5/2}$ peaks shift to 284.5 and 280.5 eV, respectively, and the O_{1s} peak shifts from 530.7 to 533.3 eV. However, after annealing at 600 °C the intensity of the O_{1s} peak is not reduced but the binding energy shifts to a higher energy state than that of the as-deposited state. The energy shifts of Ru_{3d} and O_{1s} mean that O atoms break off the binding force with Ru atoms and the binding energy of O atom shifts to higher energy, whereas Ru peaks shift to lower binding energies.[9] This result is consistent with the RBS result where the O/Ru ratio decreases from 2.2 to 2.0 during the annealing processes. Futhermore, the relative XPS intensities of double peaks of Ru_{3d} are given by the ratio of their respective degeneracies $(2j+1)$ and the emission intensity ratio of 5/2 and 3/2 becomes 6:4 after annealing at 300 °C because the chemical formula of $RuO_{2.2}$ thin film deposited at 40 °C changes to RuO_2. Therefore, Figs. 2 and 3 suggest that the TCR of annealed RuO_x resistors is obviously insensitive to the out-diffusion of oxygen and the changes in the sign of TCR from negative to positive is also indifferent with the O/Ru ratio in the RuO_x thin films. Why then does the TCR of RuO_x thin film resistors show more metal-like properties after annealing at temperature higher than 300 °C. It should be pointed out here that the metal-like TCR behavior is closely related to the grain size of the RuO_2 thin films because the electrical resistance in the large grain is strongly increased by the phonon scattering of lattice.[10] Figure 4, where the inserted pictures are selected area diffraction (SAD) patterns, is TEM micrographs for $RuO_{2.2}$ films as-deposited and annealed at 300 and 600 °C, respectively. For the as-deposited films the grain size is small, about 30–40 Å as shown in Fig. 4(a). The SAD pattern also indicates that the as-deposited $RuO_{2.2}$ film has fine grains. Then, increasing the annealing temperature, the grain size becomes greater and greater. The grain size increases from 100–300 to 500–800 Å while the annealing temperature changes from 300 [Fig. 4(b)] to 600 °C [Fig. 4(c)]. Based on both XPS and TEM data, it is concluded that the grain growth causes the TCR of RuO_x thin film resistors to change signs from negative to positive. The higher annealing temperature gives a more positive TCR. Therefore, it could be understood, in previous works, the RuO_x films deposited at temperatures above 300 °C have positive TCR due to the large grains in the RuO_x films. The TCR of the samples annealed above 300 °C also become more positive than the TCR of RuO_x resistors as-deposited at 40 °C or annealed at below 300 °C because the electrical conductivity in polycrystalline grains is reduced mostly by phonon scattering rather than multiple scattering at impurity, defect and grain boundaries. But, the RuO_x resistor as-deposited or annealed at below 300 °C behaves like a semiconductor because the grain size is so small that the electron transport is critically limited by numerous grain boundaries.[11] The main path for electron transport in the microcrystalline grains is tunneling through the grain boundaries and the mobility increases with higher temperatures. Therefore, the TCR of microcrystalline RuO_x thin film resistor becomes gradually negative, which is similar to the TCR characteristics of a semiconductor.

In summary, the changes in negative to positive TCR for RuO_x thin film resistors were quantitatively and qualitatively analyzed with RBS, *in situ* XPS and TEM as well as electrical resistance measurements. A near zero temperature coefficient of resistance (TCR) about 0 ± 0.12 ppm/°C can be realized for the $RuO_{2.2}$ film resistors deposited at 40 °C and post-annealed at 300 °C for 30 min in an Ar ambient. RBS and *in situ* XPS clearly show that the decrease in the O/Ru ratio makes no difference in the TCR, whereas the grain growth in RuO_x films causes the metal-like TCR. The change of TCR of RuO_x thin film resistors from negative to positive is mainly due to grain growth.

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