

**Stability of Conducting Amorphous Ru-Si-O Thin Films
Under Oxygen Annealing**

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Abstract

Ru₁Si₁O₄ thin films were deposited on Si and oxidized Si substrates by reactive rf magnetron sputtering of a Ru₁Si₁ target in an argon/oxygen gas mixture. 2 MeV He⁺⁺ backscattering spectrometry, four-point probe measurements and x-ray diffraction techniques were applied to study the films annealed at 700 °C in 100 % oxygen at pressures from 0.2 to 760 Torr. The as-deposited films are 180 nm thick, x-ray amorphous and have an electrical resistivity ~ 3 mΩcm. After 5 minutes of annealing at 700 °C all films show some crystallization of RuO₂. Above an annealing pressure of 8 Torr RuO₂ crystals are clearly visible by optical microscopy. The temporal evolution investigated below 0.4 Torr shows that the film resistivity drops by one half within the first 5 min. Beyond that both the resistivity and the fine-grain structure change little, if at all, for durations up to 4 h. No changes in film composition were detectable by backscattering spectrometry. Films grown on Si (111) vs. oxidized Si (100) substrates evolve identically, but an interfacial layer develops between the Ru₁Si₁O₄ film and the Si (111) substrate within the first 5 min of annealing which electrically decouples the film from the substrate.

Keywords: thin film, amorphous, ternary oxide, crystallization, oxygen influence

1. INTRODUCTION

Electrically conducting amorphous or near-amorphous thin films composed of an early transition metal, silicon, and nitrogen (TM-Si-N) have many current and pending applications. Very recently, Gasser et al. have shown that ternary films of ruthenium, silicon, and oxygen share many of the characteristics of TM-Si-N films, including a high metastability of the amorphous phase. Ru₁Si₁O₄ films obtained by reactive

sputtering of a ruthenium mono silicide target are x-ray amorphous as-deposited and remain so even after annealing for 5h at 800 °C in vacuum. [1] In oxygen at atmospheric pressure, however, the films are unstable. [2] After 30 min at 600 °C, crystallites of RuO₂ of μm in size develop out of a film originally 0.2 μm thick. Evidently, the oxygen ambient strongly affects the stability of a Ru₁Si₁O₄ film. We have undertaken to assess that influence by varying the oxygen pressure during annealing at a fixed temperature of 700 °C.

2. EXPERIMENTAL PROCEDURES

180 nm-thick x-ray amorphous films of composition Ru₁Si₁O₄ were deposited as described by Gasser et al. [2] , on two types of substrates: (i) (111) Si wafer of 16 mΩ cm resistivity, and (ii) (100) Si wafer covered with a 120 nm thick thermally grown oxide layer. The bare Si substrates were etched in dilute HF immediately prior to each deposition to minimize native oxide. Oxygen annealing was performed at 700 °C in a sealed quartz-tube furnace. The quartz-tube was evacuated and flushed several times with oxygen before filling it with oxygen to a pressure of 0.2, 8, or 760 Torr. The samples were analyzed before and after annealing with CoK_α x-ray diffractometry, 2 MeV He⁺⁺ backscattering spectrometry, four-point-probe measurements, and scanning electron microscopy.

3. RESULTS

Within the accuracy of backscattering spectrometry, the atomic composition and the depth profiles remain unchanged (< 5 %) for all annealing treatments performed at 0.2 Torr. Figure 1 compares the spectra of a film on a bare silicon substrate before and after annealing for 4 h under 0.2 Torr oxygen pressure. The small difference in the spectra at energies below 1.05 MeV are probably due to a slight channeling effect in the silicon substrate and is irrelevant in the present context. Films deposited on an oxidized silicon substrate yield the same results.

X-ray spectra reveal, however, that in spite of their constant overall composition, the films change structurally upon annealing. The higher the oxygen pressure is the more pronounced the RuO₂ crystallization becomes. Figure 2 proves this with the θ-2θ diffraction spectra obtained before and after 5 min of annealing in 0.2, 8 and 760 Torr oxygen pressure. As deposited the films are x-ray amorphous. Annealing under 0.2 Torr pressure leads to the beginning of crystallization. In addition to broad peaks resembling those present at 0.2 Torr, annealing at 8 Torr yields some sharp peaks indicating the presence

of some well-developed grains of RuO_2 . The spectrum for 760 Torr is that of a polycrystalline sample of RuO_2 . The intensities of the main peaks [(110)-32.7°, (101)-40.9° & (211)-64.0°] are consistent with a random orientation of the crystallites. The previous report that the films are stable in vacuum for 5 h at 800 °C [1] provides further support that the crystallization of the film accelerates as the oxygen pressure rises. The scanning electron micrographs of the same three samples corroborate the x-ray findings (Fig. 3 a., b., and c.). Annealing at 760 Torr for 5 min produces grain sizes ~ 3 - 7 μm while at 8 Torr the grains are 1 - 3 μm in size. Optical inspection of a sample annealed at 8 Torr for 30 min reveals that the grains are larger than on samples annealed for 5 min. Grains 0.3 - 1 μm in size can be found on the sample annealed at 0.2 Torr but their number is too small to be detected by backscattering spectrometry or x-ray diffraction.

In order to shed light on the kinetics of this crystallization process, a sample was annealed at 0.2 Torr oxygen pressure for durations increasing from 30 to 60 to 240 min and analyzed after each step. The results are shown in Fig. 4. Other samples, annealed once directly for each of these durations yielded the same result independent of the substrate. The figure also shows that most of the transformation occurs within the first 5 min of annealing; subsequent changes, if any, are slow. Whether this time dependence also applies for 8 and 760 Torr is not known but is, in our view, likely.

Grain size of the annealed samples shown in Fig. 4 was also estimated from Scherrer's formula [3] using the RuO_2 (110) x-ray diffraction peak located at $2\theta \sim 32.7^\circ$. The grain sizes obtained for the samples annealed at 0.2 Torr ranged from 2-4 nm and show no dependence on annealing duration. Fitting the sharp peaks present in the spectra of samples annealed at 8 and 760 Torr (Fig. 2) resulted in erroneous grain sizes due to the magnitude of the grains. The spectrum of the sample annealed at 8 Torr for 5 min (Fig. 2) contains superimposed sharp and broad peaks. Curve fitting to the broad peak at $2\theta \sim 32.7^\circ$ results in a grain size within the 2-4 nm range as measured also on the samples annealed at 0.2 Torr. Closer inspection of the diffraction pattern for the 760 Torr oxygen annealing did not reveal any superimposed peaks however this may be due to the lower statistics under which this particular spectrum was obtained.

A $\text{Ru}_1\text{Si}_1\text{O}_4$ film is thermodynamically unstable with excess of silicon. One hence predicts that upon annealing the film on a bare silicon substrate it will react to form SiO_2 and Ru_2Si_3 . Explicit evidence for this reaction is provided by the four-point-probe data of Fig. 5. The reported resistivity values are obtained by

assuming that the current flows only within the $\text{Ru}_1\text{Si}_1\text{O}_4$ layer. The bare (111) Si substrate is heavily doped (16 $\text{m}\Omega\text{cm}$) so that this assumption fails if the Si/layer interface is electrically transparent resulting in only a small fraction of the electric current actually flowing in the layer. This is what actually happens in the as-deposited sample and explains the low apparent resistivity of the film as deposited. After, at most, 5 min an interfacial film has developed that is thick enough to electrically decouple the film from the substrate. The data then yield the true resistivity of the film (about 1.7 $\text{m}\Omega\text{cm}$). This value agrees with that measured for a film on an insulating substrate. The figure also shows that in the latter case, the resistivity of the as-deposited film is about twice as high. A similar growth of an interfacial layer between RuO_2 and aluminum has been previously reported for annealing in vacuum. [4]

4. DISCUSSION

Annealing of $\text{Ru}_1\text{Si}_1\text{O}_4$ in vacuum above 800 °C for 30 min results in crystallization of Ru and RuO_2 . [1] The tendency to favor Ru over RuO_2 crystallization becomes more pronounced, occurring at lower temperatures, when the as-deposited films are not fully oxygenated, i.e. for $\text{Ru}_1\text{Si}_1\text{O}_{x<4}$. This trend continues until the deposited films are so depleted in oxygen that silicide formation becomes more favorable. The x-ray spectra for the oxygen annealing cycles undertaken for this study, Fig. 2 and Fig. 4, show that preferred crystallization of RuO_2 over Ru occurs. This is consistent with thermodynamic data where thermal dissociation to Ru and O_2 is not expected to occur above an equilibrium oxygen pressure of 10^{-6} Torr at 700 °C [5]. In this study we made no attempt to investigate the possibility of RuO_4 evolution from the films at our reduced annealing pressures but concede that this is possible.

Gasser et al. [1] used transmission electron microscopy and determined that as-deposited $\text{Ru}_1\text{Si}_1\text{O}_4$ films contain few RuO_2 grains 1-2 nm in size dispersed in an amorphous structure. After oxygen annealing the films, at least for the 0.2 and 8 Torr cases, seem to be composed of two distinct grain sizes. A very fine grain size possibly distributed within a still amorphous matrix, and large grains visible by optical and/or scanning electron microscopy. These two grain populations evolve differently with annealing duration and oxygen pressure. The fine grains monitored by x-ray diffractometry change little, or not at all, in size at 0.2 Torr oxygen pressure for annealing durations longer than 5 minutes. In the first five minutes these grains double in size, while the grains present on the surface of the sample grow ~ 100 – 1000 times larger than in the as-deposited films. For the same annealing duration, 5 min, at 8 Torr oxygen pressure the grains grow

1000 – 3000 times larger over the as-deposited case. In addition to this even faster growth, it is found that the large grains grow even larger for longer annealing durations. It is clear, then, that the oxygen annealing pressure plays an important role in the growth rate of the grains. However, it is still not known how the relative amounts of the two grain populations change after oxygen annealing.

The behavior of the films grown directly on Si (111) vs. oxidized Si (100) is identical. It is certain that some superficial oxidation of the Si (111) occurs prior to the film deposition either during the loading of the sample and/or during target pre-sputtering and therefore may explain the consistency of these results. We were able to minimize this oxidation sufficiently to obtain electrical conduction between the deposited film and the Si (111) substrate. Upon annealing this electrical path was severed by the growth of a SiO₂-like interfacial film.

Annealing at 0.2 Torr oxygen pressure and 700 °C results in a film with fine grains having an average size less than 10% of the film thickness and moderate low resistivity, ~ 1000 times greater than the best metal and about 100 times that of bulk RuO₂. [6] Barring the few large grains, the film is stable after the first 5 min of annealing up to at least 4 h.

5. CONCLUSION

The oxygen pressure during annealing of Ru₁Si₁O₄ films strongly influences the growth and/or crystallization of RuO₂ grains. Annealing in oxygen between 0.2 and 760 Torr at 700 °C shows that this influence is strong enough to lead to unstable films within 5 min. This instability is evidenced by the formation of μm sized RuO₂ grains. Despite this instability, beyond 5 min of annealing at 0.2 Torr oxygen at least some aspects of the film appear to be stable: namely, the resistivity and fine grain structure. Many explanations exist for this behavior. If strategies can be developed to suppress the large grain growth, the films may find use in a variety of applications.

The crystallization and/or growth of a finer grain during the first 5 min of annealing is believed to be responsible for the drop in resistivity from ~ 3 mΩcm to ~ 1.7 mΩcm of the films annealed in 0.2 Torr oxygen. Since the resistivity of bulk RuO₂ is ~ 35 μΩcm (100 times less than the as-deposited film), this drop in resistivity could be explained by an increase in the number, volume and/or proximity of these grains. However, this explanation is not entirely satisfactory without additional information regarding the microstructure of annealed films and the conduction mechanism in the as-deposited film.

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6. REFERENCES

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Fig. 1. 2 MeV He^{++} backscattering spectra of 180 nm-thick $\text{Ru}_1\text{Si}_1\text{O}_4$ film on a Si (111) substrate, as-deposited and after annealing for 4 hours in 0.2 Torr oxygen at 700 °C. The slight shift in the silicon and oxygen signals can be attributed to small changes in the beam energy, which were not accounted for in the energy conversion. (angle of beam incidence against sample normal: 7°, that of detected particles: 165°)

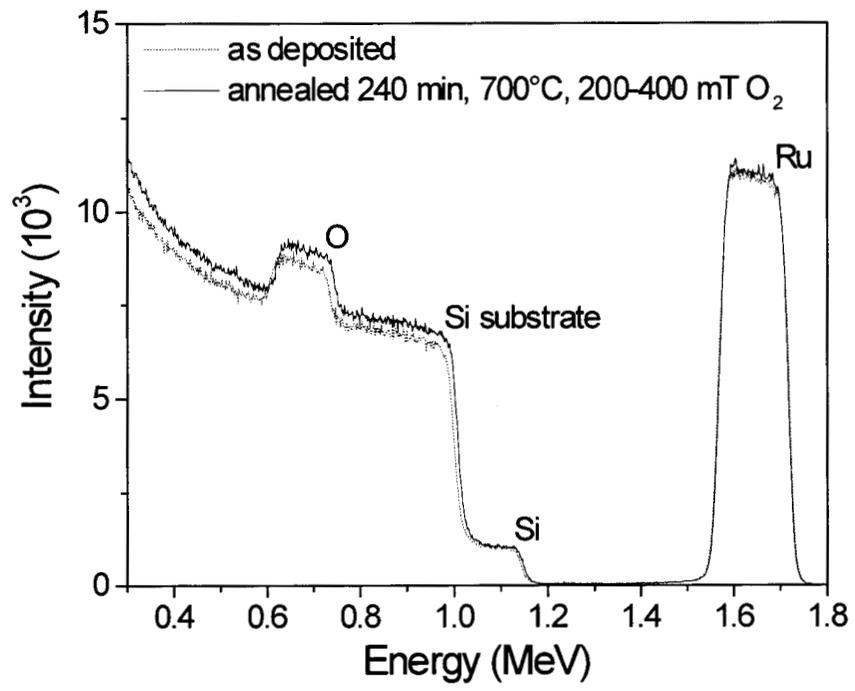


Figure 1

Fig. 2. X-ray diffraction spectra of 180 nm-thick $\text{Ru}_1\text{Si}_1\text{O}_4$ film on an oxidized Si (100) substrate, taken before and after 5 minutes of annealing at 700 °C and 0.2, 8 and 760 Torr oxygen pressure.

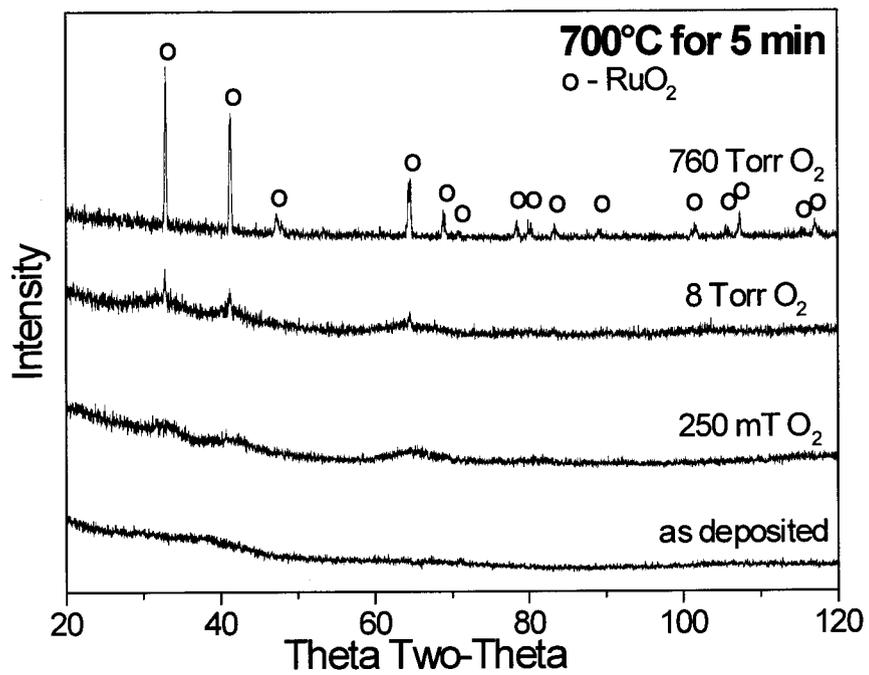


Figure 2

Fig. 3. Scanning electron micrographs taken at 10 keV of a 180 nm-thick $\text{Ru}_2\text{Si}_7\text{O}_4$ film on an oxidized Si (100) substrate before and after annealing for 5 minutes at 700 C. The oxygen pressure during annealing was a. 0.2 Torr; the grain size is $\sim 0.3 - 1 \mu\text{m}$. b. 8 Torr; the grain size is $\sim 1 - 3 \mu\text{m}$. c. 760 Torr; the grain size is $\sim 3 - 7 \mu\text{m}$.

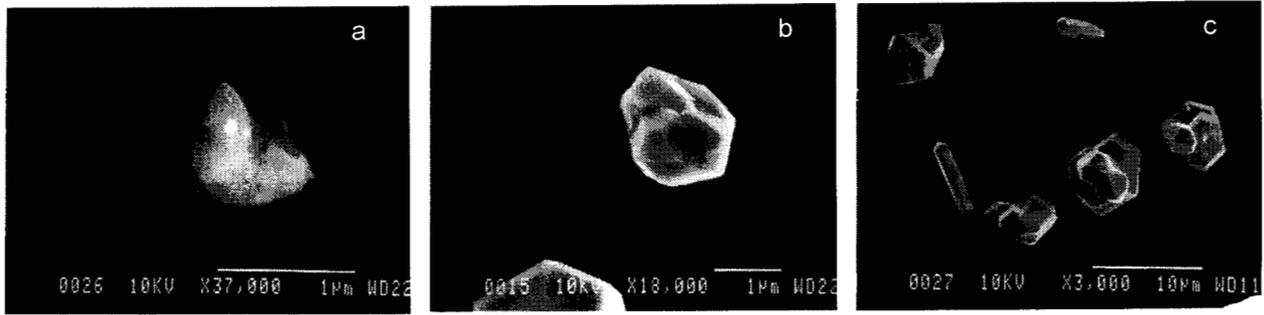


Figure 3

Fig. 4. X-ray diffraction spectra of a 180 nm-thick $\text{Ru}_1\text{Si}_1\text{O}_4$ film on an oxidized Si (100) substrate before and after annealing for 5, 30, 60 and 240 minutes at 700 °C and 0.2 Torr oxygen pressure.

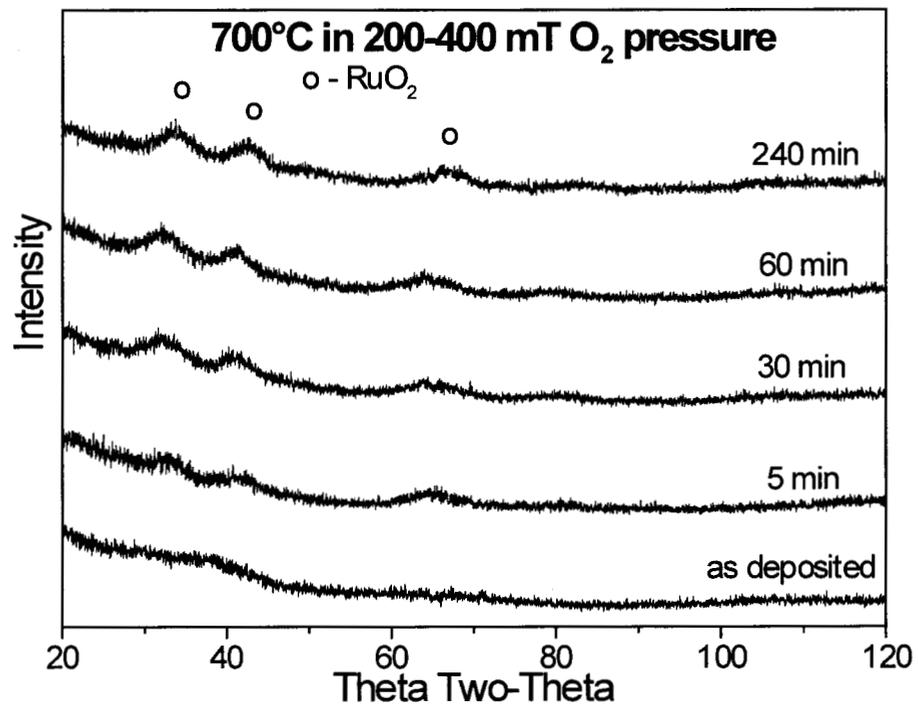


Figure 4

Fig. 5. Resistivity of 180 nm-thick $\text{Ru}_1\text{Si}_1\text{O}_4$ film deposited on an oxidized Si (100) substrate and on a Si (111) substrate before and after annealing for 5, 30, 60 and 240 min at 700 °C and 0.2 Torr oxygen pressure.

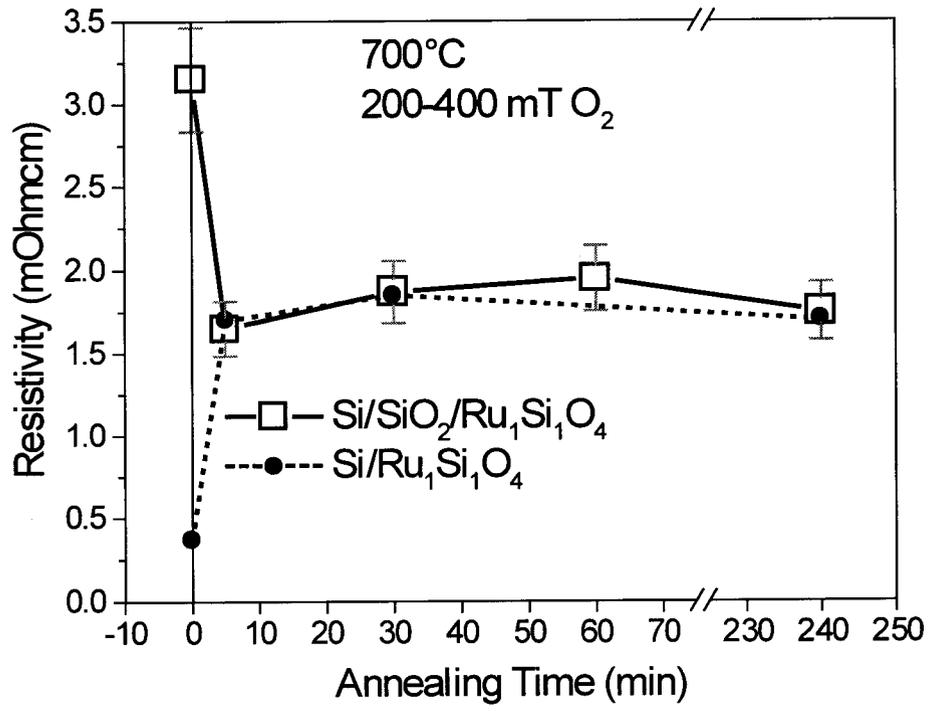


Figure 5