Instability of Amorphous Ru-Si-O Thin Films under Thermal Oxidation

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Ternary films about 200 nm thick of composition Ru$_2$Si$_{15}$O$_{65}$ have been synthesized by reactive rf magnetron sputtering of a Ru$_1$Si$_1$ target in an argon-oxygen gas. As-deposited, the films are X-ray-amorphous. Their atomic density is $8.9 \times 10^{22}$/cm$^3$ (5.1 g/cm$^3$), and their electrical resistivity is in the range of 2 m$\Omega$ cm. After annealing in dry oxygen at 600$^\circ$C for 30 min, micron-sized grains of RuO$_2$ grow out of the film and volatile RuO$_4$ escapes. The significance of these results is discussed.

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Ternary thin films of the type TM-Si-N, where TM are transition metals of the Ti, V, and Cr groups, have properties that are both scientifically interesting and practically useful. Depending on their mode of deposition, on their composition, and on their postannealing treatment, they can be structurally amorphous down to high-resolution transmission electron microscopy (TEM-amorphous), nanostructured so as to appear amorphous under X-ray diffraction (X-ray-amorphous), or polycrystalline with varying grain sizes. They can be single-phase or two-phase structured, electrically insulating or conducting. A recent compilation of the relevant literature is given in Ref. I-3. Uses where one or several unique properties of these films are exploited have been demonstrated in applications as various as a primary mask for X-ray lithography, thin-film diffusion barriers in semiconductor metallizations, and micromachining.13

Motivated by these successes, we have asked whether analogous ternary thin films of the type TM-Si-O could be synthesized with properties that might be similarly useful and interesting. This paper presents the first results and answers to this question.

Specifically, we asked if amorphous ternary films of Ru-Si-O could be obtained by reactive sputtering a Ru$_1$Si$_1$ target. This choice follows the line of thought that leads to amorphous TM-Si-N films. These alloys may be viewed as a combination of a metallogically conducting binary transition metal nitride (such as TiN, that has a simple C1 crystal structure) with Si$_3$N$_4$, an insulating nitride with a predilection for an amorphous structure, to produce a TM-Si-N film (such as Ti-Si-N). RuO$_2$ is a metallogically conducting oxide that has a simple C4 structure, and SiO$_2$ is an insulating oxide that typically forms amorphous films. In analogy with TiN and Si$_3$N$_4$, RuO$_2$ and SiO$_2$ may thus also yield amorphous ternary Ru-Si-O. Underlying this approach is the concept that a combination of species that normally solidify in different crystalline structures will frustrate the system and induce the formation of an amorphous phase. And, in addition, the combination of a predominantly metallogically bonded species with one that is predominantly covalently bonded will similarly favor that outcome. The validity of that approach is underscored by the results obtained with the TM-Si-N alloys, some of which remain X-ray-amorphous up to heat-treatments of 950$^\circ$C for 30 min in vacuum.

In the present investigation we address two particular questions about the Ru-Si-O alloy system: (i) Is it possible to obtain amorphous films by reactive sputtering of a ruthenium silicide target in an oxidizing ambient, as has been successfully done with the reactive sputtering of early transition metal silicides in a nitrogen-carrying ambient? (ii) If so, how stable are the amorphous films thus obtained upon thermal annealing? For the latter investigation, we have chosen thermal treatments in an oxidizing ambient because ruthenium can form the volatile compound ruthenium tetroxide (RuO$_4$). In contrast to annealing in vacuum, this treatment tests the stability of the resulting film both structurally as well as chemically under conditions near those encountered in practice by coatings. Amorphous conduct-
200 nm thick Ru$_{20}$Si$_{15}$O$_{65}$ film before and after annealing in dry oxygen at 600°C for 30 min. No diffraction peaks are observed from the as-deposited sample, but clear peaks emerge after oxidation. They can all be assigned to RuO$_2$. Peaks of SiO$_2$ are not detected.

The annealing also dramatically changes the backscattering spectra of the films. Figure 2 compares 2 MeV He$^{++}$ backscattering spectra of films annealed at 800°C for 5, 15, and 30 min with the spectrum of the as-deposited film. One interpretation of these spectra is that ruthenium has diffused deeply into the substrate. Another is that thick columnar features containing ruthenium have grown on or through the surface. A decrease of the total counts in the ruthenium signal upon annealing is indicated and leads to the suspicion that some ruthenium might have been lost during the oxidation process. Ruthenium tetroxide (RuO$_4$) starts to volatilize noticeably at 7°C, has a very low melting point of 25.5°C and a boiling point of 129.6°C. If RuO$_4$ were formed during the oxidation, it would be volatile and lead to the loss of ruthenium from the film.

We proved the formation of RuO$_4$ by light absorption spectroscopy. Small samples were sealed under ambient air in a Pyrex (borosilicate glass) test tube, and the test tube was annealed at 600°C for 30 min. The amount of oxygen enclosed in the test tube was sufficient to form RuO$_4$ with all the ruthenium contained in the thin film. Signs of material removal from the Ru-Si-O thin film are already seen visually by noticing that after annealing the walls of the test tube are coated with a diffuse milky layer. Figure 3 shows the absorption spectra, taken at room temperature, of the test tube before and after annealing. A clear absorption peak can be seen after annealing with its maximum around 290 nm. A main absorption maximum at 310 nm for RuO$_4$ (oxidation state $d^0$) has been published by Wells et al., while the reflectance spectrum for RuO$_2$ (oxidation state $d^4$) is reported to exhibit a broad band from 430 to 700 nm, centered at 585 nm. Accounting for the width of the peak and the resolution of the spectrometer, our result clearly proves the presence of RuO$_4$ on the walls of the test-tube and thus the loss of ruthenium from the film during annealing in dry oxygen at 600°C.

A scanning electron micrograph (SEM) of the surface of a Ru$_{20}$Si$_{15}$O$_{65}$ thin film, after oxidation at 600°C for 30 min, is shown in Fig. 4. Predominantly columnar-shaped crystallites with dimensions of about 5 µm in length and 1 µm in diameter can be observed, sticking out of a flat surface and perhaps partly embedded in it. Surface mapping by two-dimensional energy-dispersive analysis of in-
duced X-rays reveals that all the ruthenium is concentrated in the crystallites while silicon is found only in the surrounding matrix. Oxygen can be observed everywhere. Together with the X-ray data, these facts indicate that the crystallites are RuO₂. The remainder is a film of SiO₂, possibly containing some residual ruthenium oxide. The backscattering spectra of Fig. 2 are consistent with this picture. SEMs of as-deposited films on the same scale as Fig. 4 are featureless. The electrical resistivity of that film is too high to be measurable by a four-point probe.

Discussion and Conclusion

The synthesis of amorphous ternary films of composition Ru₂₀Si₁₅O₆₅ is demonstrated and confirms the idea that the combination of metallically conducting RuO₂ with covalently bonded SiO₂ leads to the formation of amorphous ternary Ru-Si-O thin films. Their electrical resistivity of about 2 mΩ cm (bulk resistivity of RuO₂: 35 mΩ cm) together with the X-ray amorphous structure makes such films acceptable candidates for applications with moderate temperature requirements.

RuO₂ is used for thin,²¹ and thick-film resistors,²²,²³ as well as for coatings on electrodes.²⁴,²⁵ Interest has recently risen for RuO₂ films as electrodes for ferroelectric barium-strontium-titanate (BST),²⁶,²⁷ and lead-zirconate-titanate (PZT),²⁸,²⁹ thin films to make nonvolatile memory elements. Films of RuO₂ have also been considered for metallizations in integrated circuits.²⁰,²¹,²² The values of the heats of formation of the transition metal oxides are comparable to those of the transition metal nitrides and indicate good thermal stability.³⁶ The surface morphology of RuO₂ films is reported to remain smooth after rapid thermal annealing up to 900°C for 10 s in argon, nitrogen, and oxygen.³⁷

On the other hand, Green et al. report that RuO₂ films disproportionate and decompose to ruthenium and volatile RuO₄ upon annealing in vacuum at 900°C for 2 h, according to the reaction 2 RuO₂ → Ru + RuO₄.³⁴ Using the process RuO₂ → RuO₂ + O₂, Yuan et al. synthesized RuO₂ films from RuO₂ by chemical vapor deposition.³⁸ In our present situation, annealing of the Ru₂₀Si₁₅O₆₅ films occurred in an open system and a dry oxygen ambient at atmospheric pressure where the supply of oxygen was unlimited. Rather than the decomposition of RuO₂ films to Ru and volatile RuO₂, we observe the formation of volatile RuO₄ and growth of RuO₂ crystallites, which is the reverse of the process described by Yuan et al. The growth of RuO₂ particles in bulk glasses was studied previously by Nakano et al.: starting with 10 vol % RuO₂ grains of around 15 nm average size dissolved in glass, extensive growth is observed only at 950°C with a particle size of 60 nm after 1 h.³⁹ In contrast, our oxygen-saturated ternary Ru-Si-O thin films separate into RuO₂ crystals and a surrounding SiO₂ matrix much more rapidly, accompanied by the evolution of volatile RuO₂. As indicated through the backscattering spectrum, major changes are observable already after 5 min at 800°C. A reaction process based on the gaseous phases of oxygen and RuO₂ appears to be most likely. Atomic oxygen has been found to etch RuO₂ to form volatile RuO₄ products.¹⁷ Other reaction processes might also be involved, since the catalytic power of ruthenium complexes is well known and used in many other fields such as solar energy conversion,⁴⁰ coordination chemistry,⁴¹,⁴² and biochemical applications.⁴³,⁴⁴

The answers to the two questions posed initially are therefore that (i) it is possible to obtain X-ray-amorphous Ru₂₀Si₁₅O₆₅ alloys by reactive sputtering of RuSi, but (ii) the alloys are unstable in an oxidizing ambient, at a temperature/temperature exposure of 30 min at 600°C or less. Our results from treatment of Ru₂₀Si₁₅O₆₅ films in oxidizing ambient do not preclude that the same films could be thermally stable in an inert ambient or vacuum. This aspect would deserve further attention.

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