

Thermal oxidation of niobium silicide thin films

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Thermal oxidation of niobium silicide thin films on oxidized silicon substrates has been investigated. The silicide films were rf sputtered from a hot-pressed alloy target of stoichiometric composition (Si/Nb \sim 2) onto heated (350 °C) substrates. Oxidation was carried out in dry and wet oxygen between 550 and 850 °C. From Rutherford Backscattering Spectroscopy (RBS) measurements, it was determined that the oxide films exhibited the same Si/Nb ratio as the initial silicide layer. While only Nb₂O₅ has been clearly identified, density considerations and experimental values of oxide thickness suggest that niobium and silicon oxides coexist. The composition of the remaining silicide layer did not change significantly during oxidation. The oxide growth was found to follow a $(t_{\text{ox}})^n$ α (time) relationship, with $n \sim 1.1$ for dry oxygen and 1.4 for wet oxygen. Activation energies of 1.9 and 1.6 eV were determined for the dry and wet oxidation processes.

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I. INTRODUCTION

The highly conductive nature of refractory metal silicides are attracting much attention as metal-oxide-semiconductor (MOS) gates and interconnections in very large scale integration (VLSI) technology.¹⁻³ In silicon gate processes, the gate electrode is usually partially oxidized to grow a high-quality oxide overlayer for isolation from other levels of metallization. Such a capability adds flexibility to the processing sequence and is a very desirable feature. Refractory metals, like molybdenum, on the other hand, because of the volatility of their oxides, cannot tolerate any oxidation. Fortunately, in general, refractory metal silicides, such as MoSi₂, WSi₂, and TaSi₂, resembles silicon in having fairly good oxidation properties.⁴⁻⁸

In this paper, we report on the thermal oxidation properties of niobium silicide thin films on SiO₂. Niobium, along with vanadium and tantalum, is a Group V A transition metal. The physical properties of its silicide thin film have been previously reported.⁹ These films consisted of mainly hexagonal NbSi₂, and to a lesser extent, the carbon-stabilized, hexagonal Nb₅Si₃ phase. The electrical resistivity was approximately 100 $\mu\Omega$ cm. The thermal oxidation of niobium silicide films reported here was performed in both dry and wet oxygen ambients.

II. EXPERIMENTAL PROCEDURE

The silicide films, 3000–4000 Å thick, were rf sputtered onto oxidized silicon substrates at 350 °C from a hot-pressed, composite target of stoichiometric proportion (Si/Nb \sim 2). Subsequently, they were oxidized in dry oxygen (UHP Grade) and wet oxygen (oxygen bubbling through water at 95 °C). After oxidation, the oxide thickness was measured with a Dektak profilometer by creating a step with photoresist and etching. Since the oxide layer was found to etch very slowly in buffered HF solution (HF:NH₄F:H₂O = 1:10:11),

more concentrated HF solutions (like those with HF:NH₄F = 1:1 and HF:H₂O = 1:1) were used. Rutherford backscattering spectroscopy (RBS), secondary ion mass spectrometry (SIMS), and x-ray diffraction were used to examine the structure and composition of the resulting films. RBS was done with a 2-MeV ⁴He⁺ beam from a linear accelerator, SIMS with a Cameca IMS 3-f ion microscope, and x-ray diffraction with a Siemens D-500 automated diffractometer.

III. RESULTS

The composition of oxidized NbSi₂ films was studied by RBS and SIMS. In Fig. 1, RBS spectra are shown for an unoxidized film and two films oxidized at 600 and 650 °C for 15 min in dry oxygen. The unoxidized silicide film is shown to be \sim 4000 Å. A Si/Nb ratio of 1.8 is calculated. Upon oxidation at 600 °C, the outermost silicide is converted to a mixed niobium/silicon oxide. The thickness ratio of the grown oxide to the consumed silicide is calculated to be \sim 2.2. The silicon-to-niobium ratio in the remaining silicide layer is \sim 2.0. For oxidation at 650 °C, the Si/Nb ratio found is 1.9. As expected, greater conversion of the silicide layer into the oxide can be observed. Given the sharp transition from the oxide to the silicide signal in the RBS spectra, an abrupt interface is probably maintained between the two layers.

To evaluate the in-depth distribution of contaminants, SIMS depth profiling was performed. The primary beam was an ³²O₂⁺ beam with an impact energy of 10.5 kV and a current density of 35 mA/cm², rastering over an 250 \times 250 μ m² area. Positive secondary ions were analyzed from an inner area of 60 μ m in diameter to eliminate the crater edge effects. ²⁸Si⁺⁺ and ⁹³Nb⁺⁺ species were sampled to represent silicon and niobium respectively in order to avoid any nonlinearities in the counts exceeding \sim 10⁶ in the electron

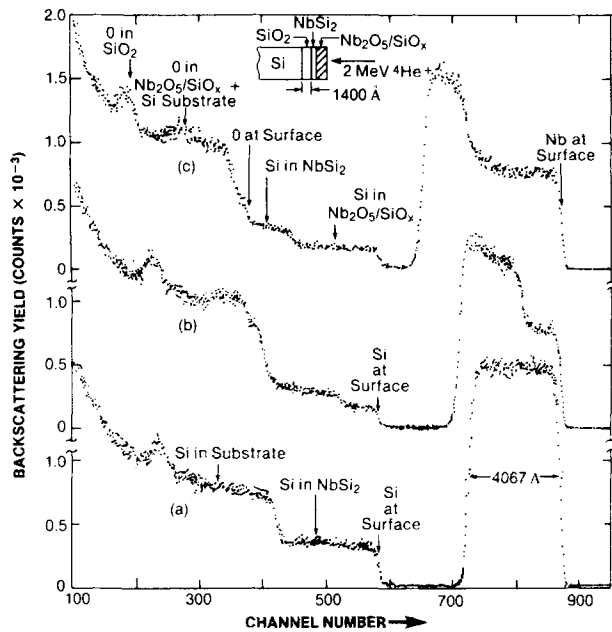


FIG. 1. RBS spectra of niobium silicide films which were (a) unoxidized, and oxidized in dry oxygen for 15 min at (b) 600 and (c) 650 °C.

multiplier. Also, to account for transmission effects, all profiles were normalized to a constant $^{28}\text{Si}^{++}$ value, enabling sample-to-sample comparisons. The depth profiles of the same films mentioned earlier revealed that the initial silicide layer as well as the subsequent oxide was relatively spatially uniform in composition (Fig. 2). The major contaminants observed by SIMS were carbon (from the sputtering target) and argon (incorporated from the ambient during sputtering).⁹ While quantitative values of carbon and argon cannot be determined without an internal standard in each matrix, one can qualitatively note an apparent increase of $^{12}\text{C}^+$ intensity as a function of oxidation [Figs. 2(a)–(c)]. Furthermore, the SIMS profiles are consistent with the RBS data, in that they show an increasing conversion of the silicide layer into the niobium/silicon oxide with increasing temperature.

X-ray diffraction measurements of the as-sputtered NbSi_2 film indicated a considerable degree of crystallinity in the film [Fig. 3(a)]. Upon oxidation at 550 °C for 15 min, no significant change in the x-ray pattern is observed. However, films oxidized at higher temperatures exhibited markedly different diffraction patterns. At 600–650 °C, most of the silicide peaks vanished and no distinct oxide peak could be identified. Since RBS results showed that both silicide and oxide exists, we can only say that both layers were essentially amorphous. At 850 °C, the diffraction pattern showed sharp peaks which can be identified with Nb_2O_5 only¹⁰ [Fig. 3(b)]. (Over twenty different forms of niobium oxides have been known to exist. Since only about six peaks were used here for indexing, our present identification is tentative.) The disappearance of the silicide at 850 °C as indicated by the x-ray pattern is consistent with the RBS results⁹ which indicated the complete oxidation of the silicide layer.

To accurately measure the grown oxide thickness, an etching solution which can selectively remove the oxide over

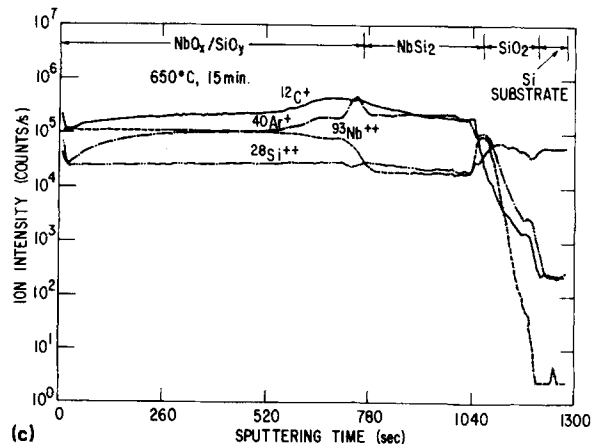
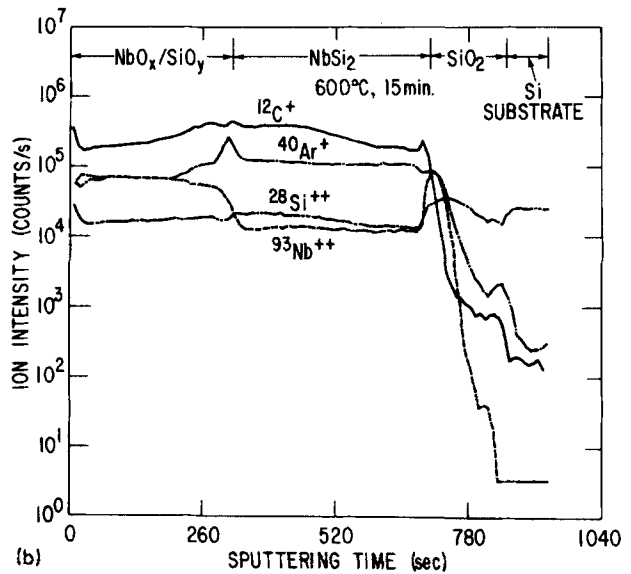
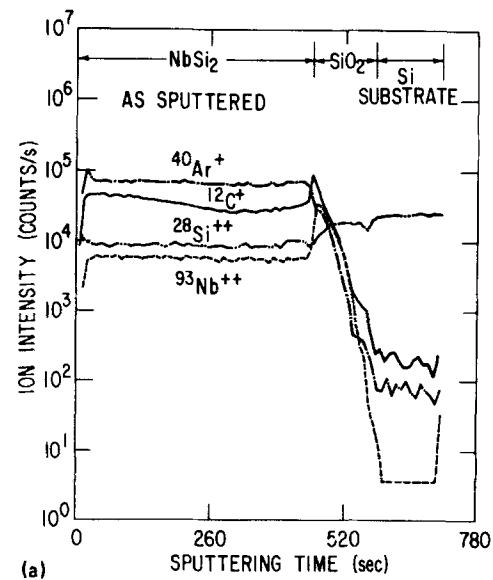


FIG. 2. SIMS depth profiles for the same films as described in Fig. 1.

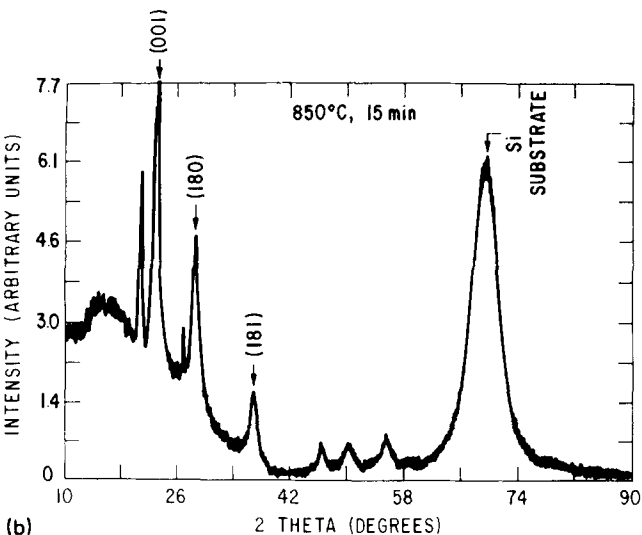
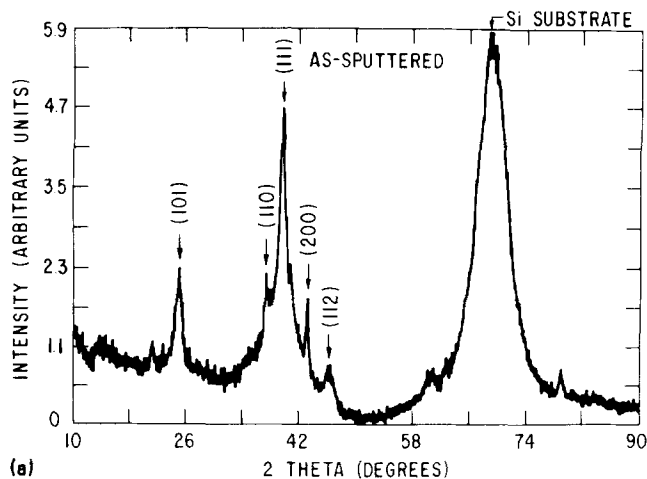


FIG. 3. X-ray diffraction patterns of (a) unoxidized and (b) oxidized (850 °C, 15 min in dry oxygen) niobium silicide thin films.

the silicide is required. As previously mentioned, buffered HF attacks the oxide layer relatively slowly, with an oxide/silicide etch rate ratio of almost unity. Satisfactory results were obtained with more concentrated HF solutions. As shown in Table I, a 50/50 HF/H₂O solution resulted in an etch rate ratio between 6 and 9. The variation in etch rate in this case is due to the depletion of fluorine ions during etching. Replacing water with NH₄F led to a twofold increase in

TABLE I. Etch rates of niobium silicide and niobium oxide/silicon oxide in various HF solutions.

Solution	Etch rate (Å/min)		Etch rate ratio (oxide/silicide)
	NbSi ₂	NbO _x /SiO _y	
Buffered HF (HF:NH ₄ F:H ₂ O = 1:10:11)	27	28	1
HF:H ₂ O = 1:1	145	900–1300	6–9
HF:NH ₄ F = 1:1	380	2150	6

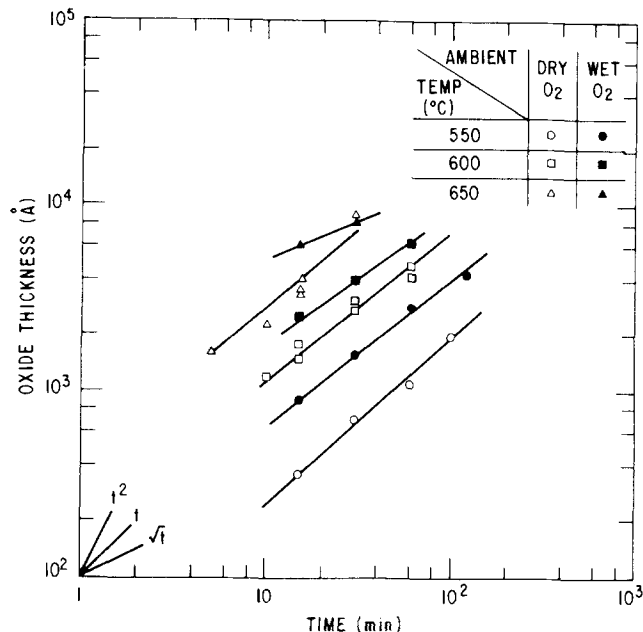


FIG. 4. Oxide thickness as a function of oxidation time in both dry and wet oxygen ambients.

etch rate, while maintaining roughly the same etch rate ratio.

The oxide thickness (t_{ox}) grown as a function of time between 550 and 650 °C is shown in Fig. 4 for both dry and wet ambients. In general, wet oxidation proceeds at a faster rate than oxidation in pure oxygen. From this data, the oxidation kinetics of NbSi₂ films can be deduced. The relationship between oxide thickness and time is seen to follow

$$(t_{ox})^n = K_0 t \exp(-E_a/kT),$$

where K_0 is a constant, t oxidation time, E_a the activation energy, k Boltzmann constant, and T temperature. Here, n ranges from ~ 1.1 for dry oxygen to ~ 1.4 for wet oxygen. When $n = 1$, the oxidation is considered reaction rate limited, while when $n = 2$, it is diffusion limited. In our case, the oxidation tends to be mostly reaction rate limited.

To determine the activation energy for the present oxidation process, the oxide thickness as a function of $1/T$ is shown in Fig. 5 for two oxidation times (15 and 30 min). In the dry oxygen case, E_a was found to be between 1.8 and 1.9 eV whereas for wet oxygen, slightly lower values (1.5–1.7 eV) were determined. Since our data do not clearly show the well-known linear-parabolic dependence on reaction time, the values of activation energy calculated should only be taken as a first-order approximation.

Even though niobium and tantalum belong to the same group in the Periodic Table, their silicides apparently oxidize very differently. While it has been reported (and recent findings^{11–13} to the contrary for cosputtered films) that sintered TaSi₂ does not oxidize in dry oxygen, we have shown that niobium silicide readily oxidize in both dry and wet oxygen at much lower temperatures. It has previously suggested¹ that since the heats of formation of oxides for the

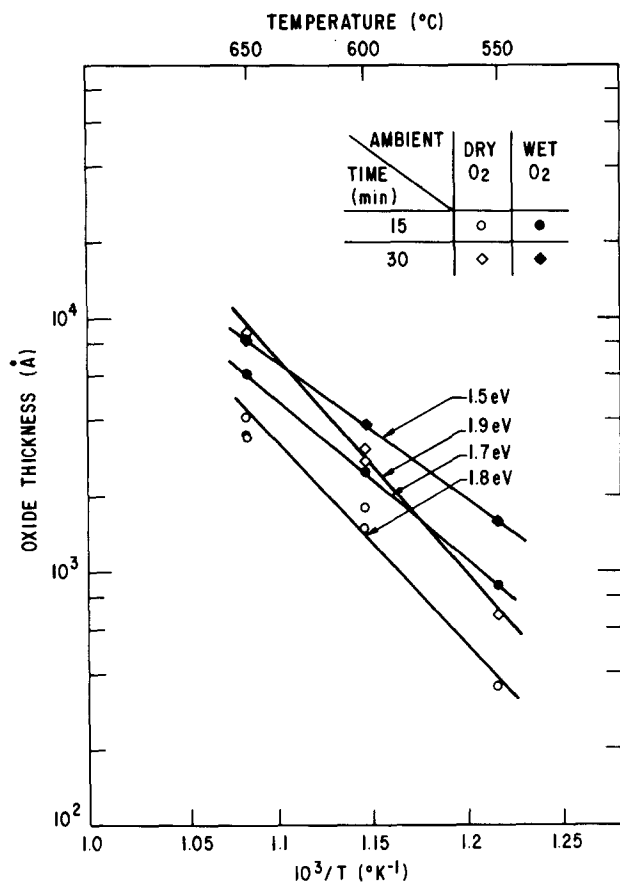


FIG. 4. Oxide thickness vs $1/T$ for silicide films oxidized in dry and wet oxygen ambients.

Group IV and V A metals are generally more negative than that for SiO_2 , the metal oxides prefer to form. [SiO_2 has $\Delta H_f(25^\circ\text{C})$ of -103 kcal per oxygen atom,¹⁴ not the value of -70 kcal/oxygen atom as shown on Fig. 8 of Ref. 1 Nb_2O_5 has a value of -93 kcal per oxygen atom. While this correction does not alter the trend for Group IV A elements, it makes the oxides from Group V A less stable than SiO_2 .] This trend has been verified in the extreme case of HfSi_2 .¹⁵ However, neither tantalum nor niobium silicide forms exclusively metal oxides under various oxidation conditions investigated so far. Therefore, other factors, such as purity of silicide film, melting or sublimation temperature of the metal oxides, diffusion rate of oxidant through the oxides, and so on, need to be considered to give a quantitative understanding of the oxidation kinetics of these silicides. These compli-

cations make the task of comparing various oxidation data very difficult at present.

IV. SUMMARY

Thermal oxidation of sputtered niobium silicide on SiO_2 has been described. The oxidation was carried out in both dry and wet oxygen between 550 and 850 $^\circ\text{C}$. The oxide layer grown had the same Si/Nb ratio as the initial silicide layer and consisted of both metal and silicon oxides. The remaining silicide layer did not change in composition. The growth rate was found to follow a $(t_{\text{ox}})^n \alpha$ (time) with n of ~ 1.1 for dry oxygen and ~ 1.4 for wet oxygen. Values of 1.9 and 1.6 eV were determined for the activation energy of the dry and wet oxidation processes, respectively.

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