Characterization of $NbSi_2$ thin films

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The physical and electrical properties of niobium silicide thin films are studied. These films were rf sputtered from an alloy target of stoichiometric proportion onto oxidized silicon substrates at 350 °C to improve film adhesion. Structural and compositional properties of as-sputtered and heat-treated films were studied by x-ray diffraction, Auger electron spectroscopy, Rutherford backscattering spectroscopy, and secondary ion mass spectrometry. Films annealed in H_2 or N_2 were found to consist of mainly $NbSi_2$ with Nb_5Si_3 as a significant component. The resistivity of these films decreases by a factor of 2 upon annealing to $\sim 1 \times 10^{-4}\ \Omega$ cm. Heat treatment in O_2 resulted in insulating films. The composition of the oxidized films was shown by both x-ray and RBS analysis to consist of Nb_2O_5 and SiO_x. $NbSi_2$-gate metal-oxide-semiconductor capacitors were fabricated on both n-type and p-type Si substrates. The work function of $NbSi_2$, determined from C-V measurements, was found to be 4.5 and 4.3 V for n-type and p-type substrates, respectively. Temperature-bias stress measurements resulted only in minor shifts in the flatband voltage, typically 0.1 V.

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I. INTRODUCTION

Severe demands are being made upon interconnection technology as device dimensions shrink with increasing levels of integration in microcircuit processing. Doped polysilicon has been used successfully for many years as the gate and interconnect material in metal-oxide-semiconductor (MOS) integrated circuits. Polysilicon can withstand the high temperature, oxidizing ambients, and chemicals used in processing. However, its resistivity of $1 \times 10^{-3}\ \Omega$ cm is becoming a problem, as line widths shrink and interconnect lengths increase. The RC product for signal transmission delay is seriously limiting the speed of very large-scale-integrated (VLSI) circuits built with polysilicon. Consequently, the use of materials other than polysilicon is being explored. Refractory metals such as molybdenum and tungsten have been investigated.[1,2] These metals have resistivities of $\sim 1 \times 10^{-5}\ \Omega$ cm and have very high melting points. However, their ability to withstand oxidizing ambients and chemicals used in processing is poor.

An attractive alternative has been found in refractory metal silicides such as $MoSi_2$ and WSi_2.[3–7] These materials have intermediate resistivities between those of polysilicon and the refractory metals. They have high melting points (> 1500 °C) and withstand the oxidizing ambients and chemicals encountered in integrated circuit processing.

This paper reports on an investigation of the physical and electrical properties of niobium silicide. Thin films were rf sputtered onto oxidized silicon substrates. The electrical resistivity of films of different thicknesses was studied as a function of annealing temperature and time in various ambients. X-ray diffraction, Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), and secondary ion mass spectrometry (SIMS) were used to investigate the film structure and composition. High frequency (1 MHz) C-V measurements were performed on $NbSi_2$-gate MOS capacitors to determine the work function on p- and n-type Si substrates.

II. EXPERIMENTAL PROCEDURE

A Veeco rf-sputtering system was used to deposit the silicide films. Details of the deposition have been described elsewhere.[8] These films were rf sputtered onto thermally oxidized silicon substrates at a power of 180 W and an argon pressure of 6×10^{-3} Torr. The typical deposition rate measured was 133 Å/min. The substrates were preheated and held at 350 °C during film deposition. This step was needed to insure film adhesion. A hot-pressed target composed of 33.37% niobium and 66.63% silicon was used. A number of samples, after silicide deposition, were also covered with 5000 Å of SiO_2. Heat treatments were performed in nitrogen, hydrogen, or oxygen ambients between 800 and 1000 °C for times up to two hours.

MOS capacitors were prepared from 5–10 Ω cm for n-type, and 8–12 Ω cm for p-type, (100) silicon wafers. A gate oxide 400–1400-Å thick was grown in dry O_2 at 1000 °C. Subsequently, 2700-Å thick $NbSi_2$ films were deposited. The backside oxide was then stripped in buffered hydrofluoric acid with a photoresist protecting the silicide film. Ion implantation, 2×10^{15} cm^{-2} of phosphorus at 140 KeV, was performed on n-type samples to ensure good ohmic contact to the back of the wafer. This implant was activated when the $NbSi_2$ films were annealed at 850 °C for 30 min in hydrogen. Plasma etching in CF_4/4% O_2 was used to obtain a pattern of dots 30 m in diameter. A barrel-type reactor (Tegal 421) was used with a positive photoresist (Shipley AZ1470) at a rf power of 100 W and a pressure of 0.2 Torr. The typical etch rate was 820 Å/min, similar to that observed for $MoSi_2$ films.[9]

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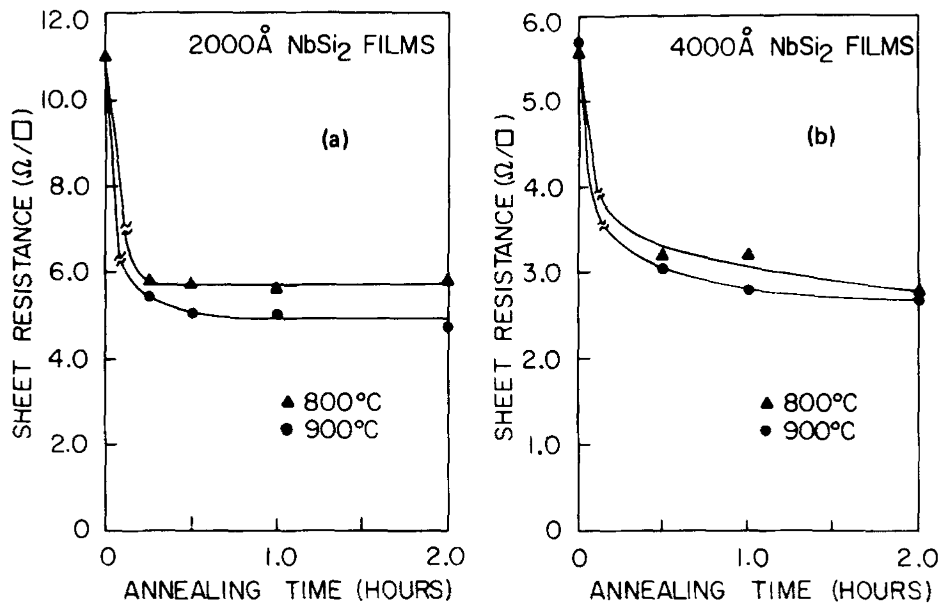

FIG. 1. Sheet resistance as a function of annealing time of $NbSi_2$ films which were (a) 2000 and (b) 4000 Å thick. The annealing was performed in nitrogen at 850 °C with an oxide cap on top of the silicide.

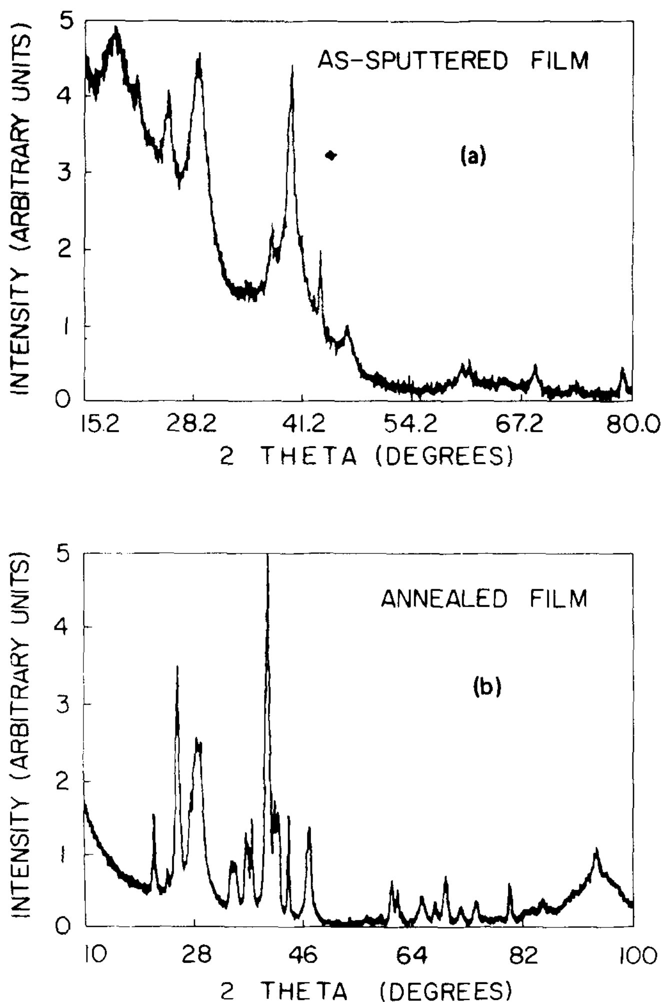

FIG. 2. X-ray diffraction patterns for a 3000-Å-thick $NbSi_2$ films which were (a) as-sputtered and (b) annealed in hydrogen at 850 °C for 30 min.

III. RESULTS

$NbSi_2$ films were annealed in N_2 and H_2 ambients over the temperature range 800–1000 °C for times between 15 and 120 min. In the case of N_2 ambient a SiO_2 cap was deposited to prevent the reaction of $NbSi_2$ with trace oxygen in the gas. This cap was subsequently removed by etching in buffered HF. This was possible due to the sufficiently high etch rate ratio between SiO_2 and $NbSi_2$.

Figure 1 shows the sheet resistance of 2000 and 4000-Å-thick $NbSi_2$ films as a function of the annealing time at 800

TABLE I. Relative x-ray intensities (peak values, corrected for background and normalized to the highest peak) of an as-sputtered, 2000-Å-thick $NbSi_2$ film.

Experimental		$NbSi_2$ [a]			Others
d(Å)	I/I_{max}	d(Å)	I/I_m	hkl	
4.17	16	4.17	11	100	
3.55	33	3.52	72	101	
3.12	69				Si(111)[b]
2.59	7	2.587	32	102	
2.40	35	2.401	19	110	
2.28	100	2.255	100	111	
2.20	37	2.199	35	003	
2.09	36	2.079	21	200	
1.95	15	1.941	64	112	
		1.621	10	113	
		1.571	4	210	
1.54	12	1.532	10	104	
		1.528	14	211	
1.51	13	1.509	12	203	
		1.418	8	212	
		1.384	4	300	
1.36	12	1.358	22	114	
		1.355	25	301	
		1.292	1	204	
		1.277	13	302	
		1.257	5	105	
1.21	12	1.200	10	220	
		1.171	3	303	

[a] Standard powder diffraction pattern 8-450.
[b] Substrate orientation.

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and 900 °C in N_2. In all cases, most of the decrease in sheet resistance occurs during the first half hour of annealing.

None of the films annealed at 1000 °C in N_2 survived. These films blistered and separated from the underlying thermal SiO_2. This is attributed to the large stress induced in the film during annealing. The adherence problem is apparently not due to a chemical reaction with the sputtered SiO_2 overlayer. Films annealed in hydrogen without a SiO_2 cap exhibited the same problem when annealed at temperatures greater than 900 °C. We believe the stress was due to a volume decrease in the recrystallization of silicide during annealing.

The $NbSi_2$ film resistivity generally decreased by a factor of 2 upon anneal to a value of $\sim 1\times 10^{-4}\ \Omega$ cm. This value is a factor of 2 larger than the value of $5\times 10^{-5}\ \Omega$ cm reported by Murarka[5] for a $NbSi_2$ film formed by sintering the metal on polysilicon. No dependence of the film resistivity on the film thickness was found.

X-ray diffraction measurements were made with a Siemens D500 Automated Powder Diffractometer. Copper $K\alpha$ radiation with a wavelength of 1.544 Å was used as the x-ray source.

Figure 2(a) shows the x-ray diffraction pattern for an as-sputtered $NbSi_2$ film. Table I shows the x-ray diffraction peaks for this sample. The peaks are listed in order of decreasing intensity. The predominant phase in the unannealed sample is hexagonal $NbSi_2$ (JCPDS card No. 8-450). The fact that the as-sputtered film, unlike $MoSi_2$[3,6] and WSi_2,[7] is not amorphous may be attributed to the heating of the substrate to 350 °C during film deposition. A strong silicon (111) peak was also present, corresponding to the orientation of the sample substrate.

Figure 2(b) shows the x-ray diffraction pattern for a $NbSi_2$ film annealed in hydrogen at 850 °C for 30 min. Table II shows the x-ray diffraction peaks for this sample. Two phases are present in the annealed film. The sample contains $NbSi_2$ (JCPDS card No. 8-450) and to a lesser extent, hexagonal Nb_5Si_3 (JCPDS card No. 8-422). The peaks are all stronger than those for the as-sputtered film, indicating a higher degree of crystallinity. Figure 3 shows the x-ray diffraction pattern for a $NbSi_2$ film oxidized in dry oxygen at 850 °C for 30 min. Table III shows the major diffraction peaks for this sample. The only crystalline phase present is Nb_2O_5 (JCPDS card No. 27-1313). Uncapped $NbSi_2$ films annealed in nitrogen were also found to oxidize to form Nb_2O_5. The trace amount of oxygen present in the 99.999% pure nitrogen used in the annealing furnace was apparently sufficient to oxidize these samples. Also, while precautions were taken, it is possible that film oxidation occurred during sample loading into the annealing furnace.

Auger electron spectroscopy measurements were made with a Physical Electronics SAM-545 Auger Analyzer. Composition-depth profiling of as-sputtered and annealed $NbSi_2$ films was achieved by combining AES with argon ion

TABLE II. Relative x-ray intensities of a 2000-Å-thick $NbSi_2$ film which was annealed for 30 min at 850 °C in hydrogen.

Experimental		$NbSi_2$ [a]			Nb_5Si_3 [b]		
d(Å)	I/I_{max}	d(Å)	I/I_m	hkl	d(Å)	I/I_m	hkl
4.15	23	4.17	11	100			
3.76	8						
3.52	65	3.52	72	101			
3.25	31				3.256	30	200
3.14[c]	47						
3.06	45				3.045	50	111
2.63	13				2.623	10	002
2.57	12	2.587	32	102			
2.46	22				2.460	50	210
					2.432	50	102
2.39	25	2.401	19	110			
2.25	100	2.255	100	111			
2.23	67				2.234	100	111
2.19	33	2.199	35	003			
					2.174	50	300
2.15	29				2.152	80	112
2.07	29	2.079	21	200			
1.94	26	1.941	64	112			
					1.631	30	400
1.63	3	1.621	10	113			
					1.586	30	113
		1.571	4	210			
1.53	12	1.532	10	104	1.531	60	222
		1.528	14	211			
1.51	10	1.509	12	203	1.497	30	320
					1.488	40	312
					1.439	50	321
1.42	17	1.418	8	212	1.424	80	213, 410
1.38	6	1.384	4	300	1.385	60	402
		1.358	22	114			
1.35	13	1.355	25	301			
1.31	5				1.311	50	004
					1.301	10	500, 322
		1.292	1	204			
					1.282	10	223
1.27	6	1.277	13	302			
		1.257	5	105	1.255	30	313, 330
					1.250	30	412
					1.232	50	420
					1.218	60	331, 204
1.20	11	1.200	10	220	1.201	10	421

[a] Standard powder diffraction pattern 8-450.
[b] Standard powder diffraction pattern 8-422.
[c] Si(111) substrate.

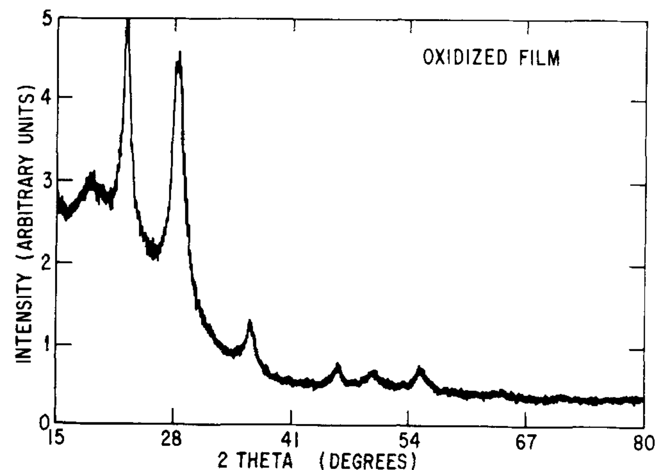

FIG. 3. X-ray diffraction pattern for a 3000-Å-thick $NbSi_2$ film which was annealed in hydrogen at 850 °C for 30 min and then oxidized in dry oxygen at 850 °C for 30 min.

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TABLE III. Relative x-ray intensities of a 2000-Å-thick $NbSi_2$ film which was first annealed for 30 min at 850 °C in hydrogen and then oxidized for 30 min at 850 °C in oxygen.

Experimental		Nb_2O_5[a]		
d(Å)	I/I_{max}	d(Å)	I/I_m	hkl
		5.22	5	130
		4.89	1	060
3.92	89	3.93	90	001
3.16[b]	100	3.15	100	180
		3.08	45	200
		3.07	16	210
		2.730	5	250
		2.608	3	260
		2.607	1	171
2.47	16	2.460	50	181
		2.428	20	201
		2.420	10	211
		2.125	3	2100
		2.118	4	1130
		2.016	6	2110
		2.013	6	330
		1.983	1	1140
1.96	11	1.969	25	002
		1.865	6	1131
1.82	11	1.832	16	0160
		1.808	1	321
		1.793	25	380, 331
		1.669	25	371, 182
1.66	14	1.660	25	0161
		1.659	25	202

[a] Standard powder diffraction pattern 27-1313.
[b] Probably included contribution from the Si(111) substrate.

milling of the sample surface. The energy of the incident primary electron beam was 5 keV. The energy of the argon ion beam was 3 keV.

Figure 4 shows the Auger electron energy spectrum of an annealed $NbSi_2$ film before and after one minute of ion milling. The sample surface shows peaks due to niobium, carbon, oxygen, and silicon. The oxygen peak is very strong. The niobium and silicon Auger peaks are much stronger inside the film while the carbon and oxygen peaks are much weaker. The bulk of the $NbSi_2$ film is seen to be relatively free of the carbon and oxygen contamination present at the film surface.

Figure 5 shows composition-depth profiles of as-sputterd and annealed niobium disilicide films which were 1000-Å thick. The peak-to-peak magnitudes of the Nb_{MNN}, O_{KLL}, and Si_{KLL} Auger peaks are plotted as a function of ion milling time. In both cases the silicide film was removed within seven minutes of ion milling. The underlaying SiO_2 layer was removed within an additional ten minutes of ion milling. The composition-depth profiles show the $NbSi_2$ and SiO_2 layers to be relatively uniform in composition.

SIMS was performed with a Cameca IMS-3-f ion microscope to study as-sputtered and hydrogen annealed silicide films 3000 Å thick. The relative intensities of various ion species—niobium ($^{93}Nb^+$), silicon ($^{28}Si^{++}$), argon ($^{40}Ar^+$), carbon ($^{12}C^+$), and hydrogen ($^1H^+$)—are measured as a function of milling time, as shown in Figs. 6(a) and 6(b). The annealed sample analyzed was previously heat treated in hydrogen at 850 °C for 30 min, decreasing its sheet resistance from 8.1 to 3.5 Ω/□. From the SIMS profiles it can be observed that the relative amounts of ion species are essentially the same in both films. Apparently post-deposition annealing under these conditions affects only the crystal structure and hence the electrical properties, but not the relative atomic composition, including the contaminants.

The SIMS data also indicate a fairly constant Nb/Si ratio throughout both films. The main impurity detected was argon which was used for film deposition and estimated to be a few atomic percent. Carbon was also present, though to a lesser degree. Argon and carbon were also the main impurities in $MoSi_2$ films sputtered from alloy targets.[10] Annealing in the hydrogen ambient did not result in a signifi-

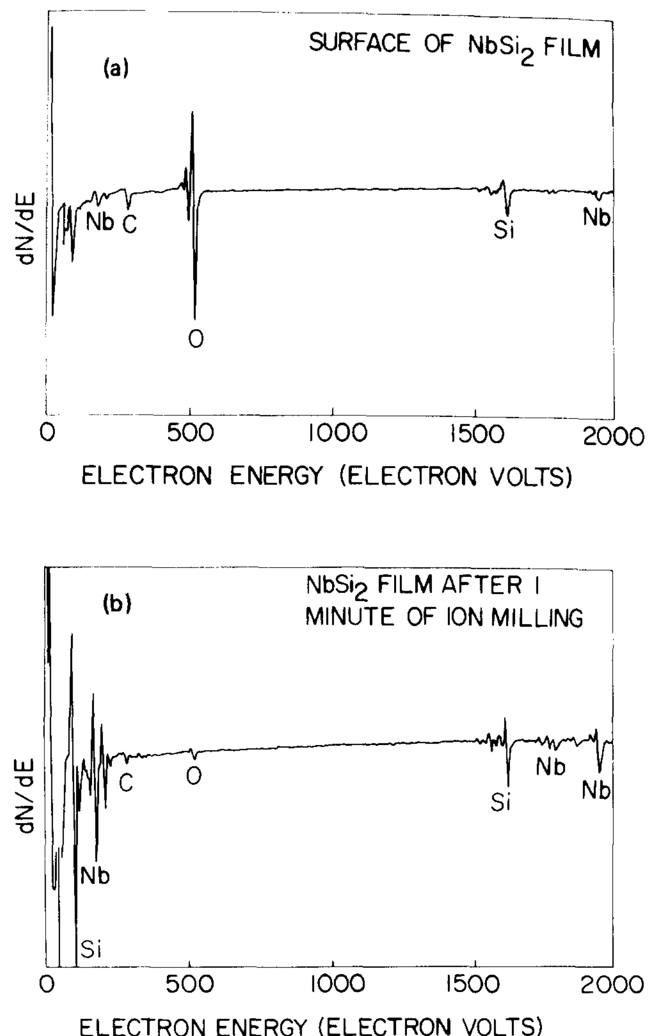

FIG. 4. Auger spectra of a 1000-Å-thick $NbSi_2$ film which was annealed in hydrogen at 850 °C for 30 min. The spectra were taken for (a) as-is surface and (b) after 1 min of ion milling with argon.

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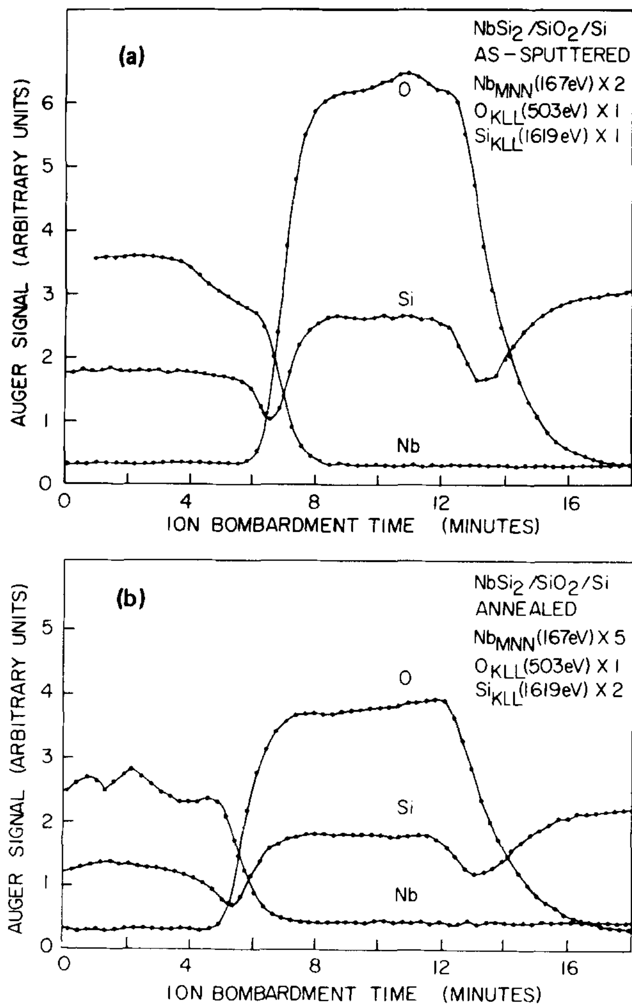

FIG. 5. Auger depth profiles of 1000-Å-thick $NbSi_2$ films which were (a) as-sputtered and (b) annealed in hydrogen at 850 °C for 30 min.

cant change in the relative amount of hydrogen present. Furthermore, one can also infer that there is little or no interfacial reaction between $NbSi_2$ and SiO_2, as the constituent profiles remain constant upon the present annealing conditions. Finally, the amount of oxygen present could not be determined from the SIMS analysis, as it was the species used for ion milling. However, the Auger analysis mentioned earlier indicated relatively insignificant amounts of oxygen within the films.

RBS was used with 2-MeV $^4He^+$ ions to further examine the 2000-Å-thick, as-sputtered and hydrogen annealed silicide films, as well as that of films further oxidized in dry oxygen at 850 °C for 30 min after annealing. The RBS spectra for the as-sputtered and annealed films (not shown) differ very little from one another, confirming the stability of atomic composition upon annealing, as revealed earlier in the SIMS data. Furthermore, the Si/Nb ratio was fairly uniform throughout the silicide layer and estimated to be 1.72. From this, it was estimated that 80% of the silicide film consists of $NbSi_2$, assuming the remainder being Nb_5Si_3. Only these two phases were detected by x-ray diffraction measurements as reported above.

Upon oxidation at 850 °C for 30 min, the resulting films were found to be insulating and lost their specular metallic appearance. The RBS spectrum, shown in Fig. 7, suggests the complete oxidation of the silicide layer, forming a mixed niobium oxide/silicon oxide layer. This is because oxygen, niobium, and silicon were all detected on the sample surface as well as the fact that the niobium and silicon signals remain fairly constant throughout. The niobium oxide phase present, as pointed out earlier in the x-ray measurements, was Nb_2O_5. The Si/Nb ratio apparently did not change after oxidation, indicating that there was no significant loss of metal. This observation is also consistent with the high melting point (1485 °C) observed for Nb_2O_5. The Nb:Si:O ratio was estimated to be 1:1.7:8, implying the complete consumption of the original silicide film. It is worth noting that these remarks apply to the oxidation of $NbSi_2$ films on SiO_2 only. Work on oxidation of silicide films on monocrystalline and polycrystalline silicon is now in progress.

The rapid oxidation behavior of the niobium silicide on SiO_2, observed for the relatively low temperature and short

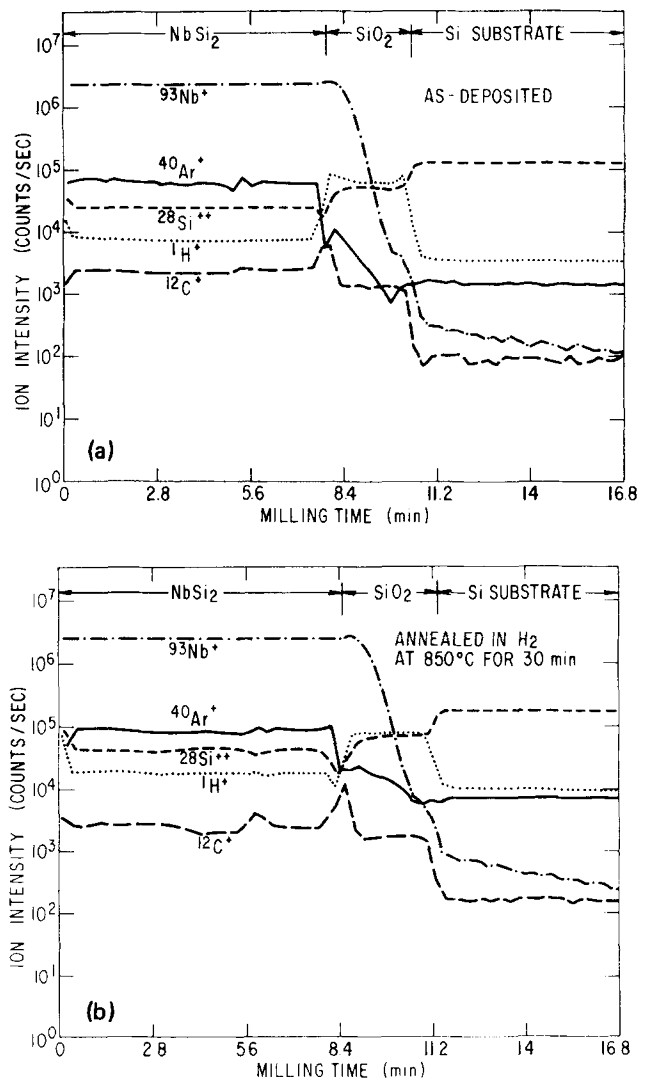

FIG. 6. SIMS depth profiles of 8000-Å-thick $NbSi_2$ films which were (a) as-deposited and (b) annealed in hydrogen at 850 °C for 30 min.

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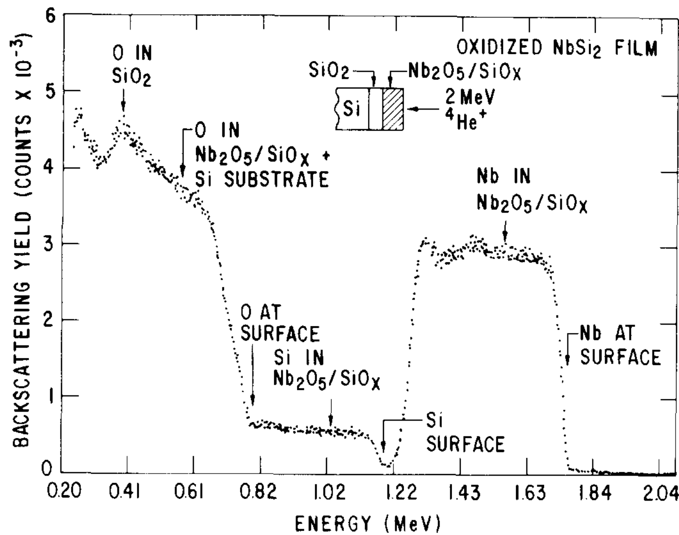

FIG. 7. RBS spectrum of an oxidized niobium silicide film on an SiO_2/Si substrate. The oxidation was carried out in dry oxygen at 850 °C for 30 min after being first annealed in hydrogen at 850 °C for 30 min.

time used, make it resemble that of $HfSi_2$[11] rather than those of $TaSi_2$,[12] WSi_2,[13,14] or $MoSi_2$.[15,16] The free energy considerations, suggested by Murarka,[5] predict that niobium, not silicon, is preferentially oxidized, and hence niobium oxide is formed in our case while for $MoSi_2$ (or WSi_2) SiO_2 tends to be favored. However, these explanations would correctly separate $NbSi_2$ from WSi_2 and $MoSi_2$, but group it with $TaSi_2$ which does not oxidize significantly in dry oxygen.[14] Hence, other factors, such as melting and sublimation temperature of these transition metal oxides as well as the diffusion rate of oxygen through the oxides, have to be included in order to give a quantitative understanding of the oxidation kinetics of these silicides. Clearly, more work needs to be done to elucidate the oxidation mechanisms for various silicides. Furthermore, the effect of impurities like argon and carbon on oxidation has been mentioned[17] but not yet fully understood.

Turning now to the electrical results, *C-V* measurements were made on $NbSi_2$-gate MOS capacitors to determine threshold stability and the work functions of $NbSi_2$.

Bias-stress tests were performed by applying a gate bias of 10 V for a period of 15 min at a substrate temperature of 150 °C. The results showed only minor shifts in the flatband voltage, typically 0.1 V or less for both *n*- and *p*-channel devices. This indicates an acceptable amount of mobile charge present in the structure. For example, taking the case of a *p*-MOS structure with 1100 Å of SiO_2, the effective mobile ion density in the oxide is calculated to be $2\times10^{10}/cm^2$.

The high frequency capacitance-voltage techniques were used to determine the metal to semiconductor work function difference ϕ_{MS}.[18] For an *n*-type substrate ϕ_{MS} is given by

$$\phi_{MS}=\phi_M-\left(\chi+\frac{E_G}{2}-\psi_N\right), \tag{1}$$

where ϕ_M is the metal work function, χ is the silicon electron affinity, E_G is the silicon band gap, and ψ_N is the difference between the bulk Fermi level and the intrinsic Fermi level.

Similarly, for a *p*-type substrate, ϕ_{MS} is given by

$$\phi_{MS}=\phi_M-\left(\chi+\frac{E_G}{2}+\psi_p\right), \tag{2}$$

where ψ_p is the difference between the bulk Fermi level and the intrinsic Fermi level. At thermal equilibrium, ϕ_{MS} is related to the flatband voltage according to

$$V_{FB}=\phi_{MS}-\frac{Q_{ss}d_{Ox}}{\epsilon_{Ox}\epsilon_0}, \tag{3}$$

where Q_{ss} is the effective fixed oxide charge density at the SiO_2/Si interface, d_{Ox} the SiO_2 thickness, and ϵ_{Ox} the SiO_2 dielectric constant. ϕ_{MS} was determined experimentally for $NbSi_2$ by plotting V_{FB} as a function of d_{0x}. Extrapolation of the flatband voltage to a zero oxide thickness yields ϕ_{MS}, assuming Q_{ss} is constant. Since all the samples were processed in the same manner we expect that Q_{ss} was indeed constant.

The depletion approximation was invoked to determine the flatband voltages from the *C-V* plots.[19] The ratio of the capacitance at the flatband to the accumulation capacitance (oxide capacitance) is given by

$$\frac{C_{FB}}{C_{Ox}}=\frac{1}{1+\dfrac{\epsilon_{Ox}\epsilon_0}{d_{Ox}q}\left(\dfrac{kT}{\epsilon_{Si}\epsilon_0 N}\right)^{1/2}}, \tag{4}$$

where ϵ_{Si} is the silicon dielectric constant and N is the impurity doping concentration. d_{Ox} was determined experimentally from the measured accumulation capacitance and the area of the $NbSi_2$ dots. Values for d_{Ox} were checked by direct measurement with an ellipsometer. The surface state density N_{ss} was determined from the slope of the V_{FB} vs d_{Ox} plot as

$$N_{ss}=\frac{Q_{ss}}{q}=-\frac{\epsilon_{Ox}\epsilon_0}{q}\frac{\partial V_{FB}}{\partial d_{Ox}}. \tag{5}$$

Capacitance-voltage measurements were performed using a Princeton Applied Research 1-MHz *C-V* plotter with a voltage ramp rate of 100 mV/s over the range -5 to $+5$ V.

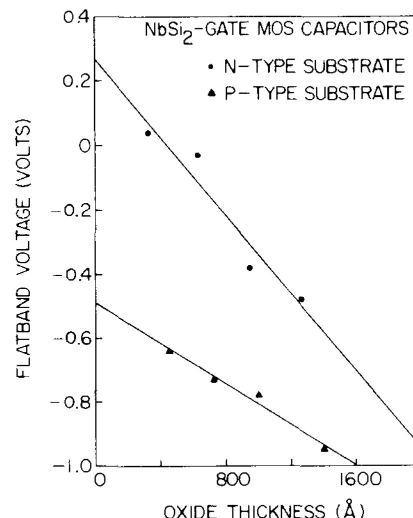

FIG. 8. Flatband voltage as a function of oxide thickness for *n*- and *p*-type channel $NbSi_2$-gate MOS capacitors.

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TABLE IV. Comparison of several refractory metal and metal silicide work functions.

Silicide	Silicide work function	Metal work function[e]
$TiSi_2$	3.67–4.25[a]	4.33
$TaSi_2$	4.15[a]	4.15–4.25
$MoSi_2$	4.6 –4.8[b]	4.53–4.6
WSi_2	4.55–4.8[c]	4.55–4.63
$NbSi_2$	4.35–4.53[d]	4.02–4.3

[a]Ref. 20.
[b]Ref. 3.
[c]Ref. 18.
[d]This work.
[e]Ref. 21.

Figure 8 shows plots of flatband voltage as a function of oxide thickness for n- and p-channel MOS capacitors. The lines shown are least squares fits to the data points for d_{Ox} as determined from the accumulation capacitance. The extrapolation to zero oxide thickness gives $\phi_{MS} = 0.27$ V for n-type substrates, and $\phi_{MS} = -0.49$ V for p-type substrates. Therefore, taking $E_g/2 = 0.55$ V and $\chi = 4.00$ V, we have $\phi_M = 4.53$ V for n-type substrates and $\phi_M = 4.35$ V for p-type substrates. From the flatband voltage data surface state densities of 1.18×10^{11} cm^{-2} and 5.7×10^{10} cm^{-2} were obtained for p- and n-channel devices, respectively.

The work functions obtained here are compared with those of other refractory metal silicides as well as those of the corresponding metals. The results are shown in Table IV. It can be pointed out that $NbSi_2$ is similar to the other silicides in following the general trend that the metal and metal silicide work functions are nearly the same. Also, comparing them with n^+ doped polycrystalline silicon which has a value of 4.2 eV, silicides have nearly the same or higher (by as much as 0.6 eV) values. Consequently, silicide-gate MOS devices will have a higher threshold in the n-channel case and a lower one in the p-channel case, if the process parameters are kept the same as the Si-gate devices. Fortunately, ion implantation can be easily employed to adjust the thresholds to the desired values.

IV. SUMMARY

Thin film properties of niobium silicide films prepared by rf sputtering from a stoichiometric proportion alloy target have been investigated. It was found that preheating to 350 °C and annealing at temperatures lower than 1000 °C is necessary to ensure film adhesion. X-ray diffraction and RBS revealed that, upon annealing, the silicide film was mostly $NbSi_2$, with Nb_5Si_3 as a significant component, with a concurrent decrease in resistivity to 1×10^{-4} Ω cm. Upon oxidation in dry oxygen the silicide was rapidly converted into mixed niobium oxide/silicon oxide. SIMS and Auger depth profiles suggested compositional uniformity and little interfacial reaction with the underlying SiO_2 for silicide films annealed at 850 °C for 30 min. Argon and carbon were found to be the main contaminants. These silicide films were overall compatible with standard MOS processing, except that buffered HF solution was seen to etch them slowly. Extra precautions were also necessary to maintain an ultrahigh purity, inert ambient for the heat treatment so as to avoid drastic film degradation. The work functions of $NbSi_2$ have been determined to be 4.5 and 4.3 V for n-type and p-type Si substrates, respectively, from C-V measurements on MOS capacitors. Temperature-bias stress measurements resulted only in minor shifts in the flatband voltage, confirming the accuracy of the work function values.

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[1]D. M. Brown, W. E. Engeler, M. Garfinkel, and P. V. Gray, J. Electrochem. Soc. **115**, 874 (1968).
[2]F. Yanagawa, K. Kiuchi, T. Hosoya, T. Tsuchiya, T. Anazawa, and T. Mano, IEEE Trans. Electron Devices **27**, 102 (1980).
[3]T. Mochizuki, K. Shibata, T. Inoue, and K. Ohuchi, Jpn. J. Appl. Phys. **17**, 37 (1978).
[4]B. L. Crowder and S. Zirinsky, IEEE Trans. Electron Devices **26**, 369 (1979).
[5]S. P. Murarka, J. Vac. Sci. Technol. **17**, 775 (1980).
[6]T. P. Chow and A. J. Steckl, Appl. Phys. Lett. **36**, 297 (1980).
[7]F. Mohammadi and K. C. Saraswat, J. Electrochem. Soc. **127**, 450 (1980).
[8]C D. Rude, "Characterization of $NbSi_2$ Thin Films," MS thesis, Rensselaer Polytechnic Institute, May 1980.
[9]T. P. Chow and A. J. Steckl, Appl. Phys. Lett. **37**, 466 (1980).
[10]T. P. Chow (unpublished).
[11]S. P. Murarka and C. C. Chang, Appl. Phys. Lett. **37**, 639 (1980).
[12]S. P. Murarka, D. B. Fraser, W. S. Lindenberger, and A. K. Sinha, J. Appl. Phys. **51**, 3241 (1980).
[13]S. Zirinsky, W. Hammer, F. d'Heurle, and J. Baglin, Appl. Phys. Lett. **33**, 76 (1978).
[14]F. Mohammadi, K. C. Saraswat, and J. D. Meindl, Appl. Phys. Lett. **35**, 529 (1979).
[15]T. Inoue and K. Koike, Appl. Phys. Lett. **33**, 826 (1978).
[16]T. Mochizuki and M. Kashiwagi, J. Electrochem. Soc. **127**, 1128 (1980).
[17]J. Rouse, F. Mohammadi, C. R. Helms, and K. C. Saraswat, Appl. Phys. Lett. **37**, 305 (1980).
[18]K. C. Saraswat and F. Mohammadi, IEEE Electron Device Lett. **1**, 18 (1980).
[19]W. Werner, Solid-State Electron. **17**, 769 (1974).
[20]F. Mohammadi, Solid-State Tech. **24**, 65 (1981).
[21]H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).

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