Thermal oxidation of nickel disilicide

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The thermal oxidation characteristics of nickel disilicide on Si substrates have been investigated in the temperature range of 700–900 °C in dry oxygen and wet oxygen. A surface layer of SiO_2 grows parabolically in time. The growth rate is independent on the crystalline structure (epitaxial or polycrystalline) and thickness of the $NiSi_2$ layer. We surmise that the oxidation mechanism is dominated by oxygen diffusion through the growing SiO_2. Activation energies for the dry and wet oxidation are 1.0 ± 0.1 eV and 1.5 ± 0.1 eV, respectively. $NiSi_2$ layers on SiO_2 oxidize with the same rate—resulting with progressively Ni-rich $NiSi_2$. Preliminary measurements of the oxide quality yield dielectric strength of 2.1×10^6 V cm^{-1}, and a pinhole density of about 100 per cm^2. A survey of oxidation data for Si and other refractory metal silicides shows that their oxidation does not draw similar kinetics to that of $NiSi_2$.

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Refractory metal silicides have been extensively explored as possible material for integrated circuit interconnects.[1,2,3] Two of the most important desired properties for such a material are a low resistivity and the possibility to form a thermal oxide. The resistivity of $NiSi_2$ is 40–60 $\mu\Omega$ cm[1,4] compared to 400 $\mu\Omega$ cm for highly doped poly-Si as is currently used. This makes $NiSi_2$ an attractive material for the desired purpose. The formation of an insulating layer of SiO_2 is important for isolation, passivation, and photolithography. In this context, it is therefore of interest whether $NiSi_2$ (not refractory, melting point 993 °C, lowest eutectic temperature 966 °C) can be oxidized. The eutectic temperature of 966 °C limits subsequent processing to temperature of about 900 °C. This limit is no hindrance, since the metallization step comes after the completion of all diffusion steps, and it is then desired to keep processing temperatures low in order to minimize further diffusion. In this letter, we explore the thermal oxidation of $NiSi_2$ and characterize the SiO_2 growth kinetics.

Nickel films were deposited onto ⟨111⟩ *n*-type Si substrates using a dry-pumped *e*-gun evaporator. The pressure during deposition was less than 2×10^{-7} Torr. The vacuum annealing was performed at a pressure less than 10^{-6} Torr at 400 °C for 30 min, and was followed by ramping the temperature up to 800 °C for 20 min; a further annealing at 800 °C for 15 min completed the film preparation by transforming all the Ni to $NiSi_2$. We confirmed by backscattering spectroscopy (BS) and channeling measurements that $NiSi_2$ layers thus formed were single crystalline in nature.[5] Additional samples were prepared on poly-Si. For these samples, a thick (1600 Å) layer of amorphous silicon was initially *e*-gun evaporated at a pressure less than 3×10^{-7} Torr on ⟨Si⟩ substrates, followed by Ni deposition without breaking vacuum. These samples were then annealed in the way described above to form $NiSi_2$. Since the amorphous deposited Si turns into a polycrystalline structure while silicide grows, one expects the $NiSi_2$ layer to be polycrystalline. X-ray diffraction pattern of the $NiSi_2$ confirmed the polycrystalline nature of these layers.

The oxidation was performed under two different conditions: dry O_2 atmosphere and wet O_2 (bubbled through 95 °C H_2O). The oxide film was measured by 2-MeV $^4He^+$ BS. These measurements gave a stoichiometric ratio of 1 to 2 (within the accuracy level of BS measurement) for Si to oxygen, indicating that the oxide is SiO_2. The SiO_2 thickness was calculated, assuming an SiO_2 density of 2.27 g cm^{-3}.[6] The use of 2-MeV He enables us to assume the "classical" vapor values of stopping power[7] of an oxygen atom for our energy range.[8]

The first issue we address is the dependence, if any, of the oxidation process on the $NiSi_2$ film thickness. Samples with Ni thicknesses of 500 and 1400 Å were prepared on Si ⟨111⟩ substrates, and with 750-Å Ni thickness on 1600 Å amorphous on ⟨Si⟩. The samples were then thermally transformed to $NiSi_2$ layers with thicknesses of 1750, 5000, and 2650 Å, respectively. These samples were oxidized at 900 °C for a duration of 15 min to 2 h in wet oxidation, and for 1 h up to 12 h in dry oxidation.

All samples, regardless of their initial $NiSi_2$ thickness, grew exactly the same thickness of SiO_2 for a given time of oxidation. This fact suggests that the growth is controlled by the SiO_2, either in the bulk (diffusion) or at the interfaces (reactions), or both, but not by transport across the silicide layer. The fact that samples prepared on poly-Si or on ⟨Si⟩ have the same oxidation rate also shows that the structure and orientation of the substrate Si at the Si/$NiSi_2$ interface is of no consequence.

Since the main interest in $NiSi_2$ films for integrated circuits is for interconnections, we evaporated Ni on thin poly-Si which was deposited on SiO_2. This situation is close to real usage in integrated circuits. About 2400 Å of poly-Si were *e*-gun evaporated on SiO_2 substrate, followed by 500-Å-thick Ni layer. After the annealing step, one would expect 1850 Å of the poly-Si to be consumed by the interaction with the Ni, which would leave about 550 Å of unreacted poly-Si. We did not observe a sharp interface between $NiSi_2$ and the poly-Si, which is probably due to Ni diffusion into the poly-Si layer through grain boundaries. (The same observation was made for the polycrystalline samples on Si.) Again, the silicide formed was polycrystalline in nature compared to the single-

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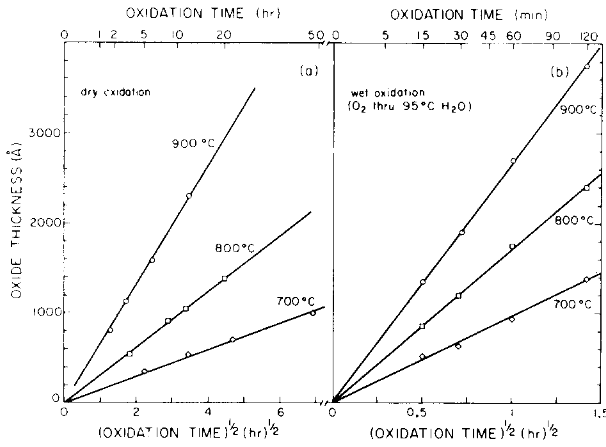

FIG. 1. Thickness of SiO_2 layer grown thermally on $NiSi_2$ on a ⟨Si⟩ substrate for (a) dry oxidation and (b) wet oxidation at 700, 800, and 900 °C as a function of time. The thickness depends parabolically on time.

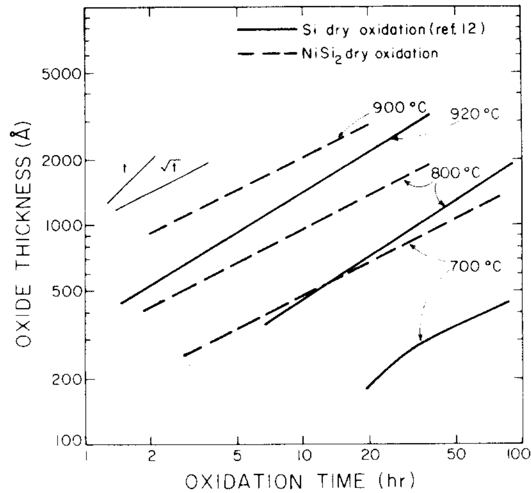

FIG. 3. Comparison between dry oxidation of ⟨Si⟩ and $NiSi_2$.

crystal epilayer of $NiSi_2$ that form on ⟨Si⟩.[5] These samples were then oxidized. The oxide thickness grown was exactly the same at 900 °C, wet or dry, for equal oxidation times, as that of all the other samples with different $NiSi_2$ thicknesses or crystalline structure. However, these new samples had a limited supply of Si underlying the layer. Once the oxidation process had consumed all the underlying Si, a change in the oxidation rate was anticipated. In our samples, this situation should occur for an oxide thickness above 1200 Å. For oxides thicker than that, we found from BS that the stoichiometric ratio in the $NiSi_2$ changed toward increasingly Ni-rich silicide. But measurements of the oxidation kinetics yielded a constant oxidation rate for an oxide thickness up to 3700 Å. At that oxide thickness, in addition to the remaining 550 Å of poly-Si, approximately 60% of the $NiSi_2$ layer was oxidized. This oxide growth was not accompanied by any

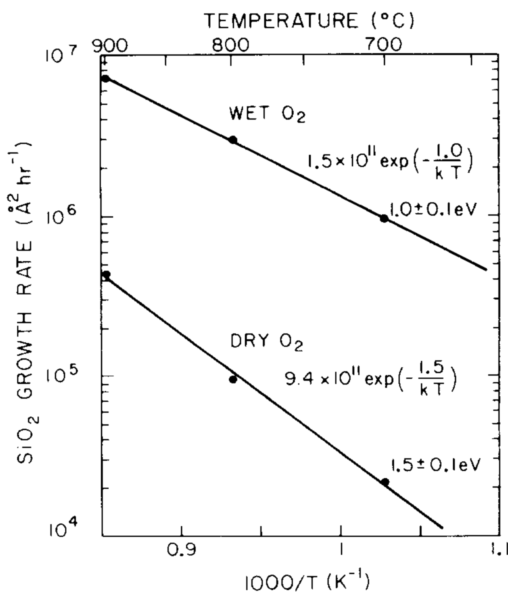

FIG. 2. Arrhenius plot of oxide growth rates on $NiSi_2$ for dry and wet oxidation.

detectable trace of NiO_x. The Ni-rich silicide thus oxidizes at the same rate as the stoichiometric $NiSi_2$ on excess silicon.

Having established the fact that the oxide growth is independent of the $NiSi_2$ thickness, structure, or even stoichiometric ratio of the silicide, enabled us to carry on the analysis of the kinetics with one specific Ni thickness. We used 500-Å Ni on ⟨111⟩ Si substrate for those oxidations that were performed at 800 and 700 °C under dry and wet conditions. Figure 1 summarizes the results of those oxidations under dry O_2 conditions (a), and wet oxidation (b). It is clear that the reaction has a parabolic time dependence (thickness is proportional to $\sqrt{t}$). The kinetics of the reaction can be fitted to the following equation:

$$d^2 = K_0 \exp(-E_a/kT)t, \qquad (1)$$

where t is the growth time, d is the SiO_2 thickness, E_a is the activation energy, k is the Boltzmann constant, T the absolute temperature, and K_0 is a proportionality constant related to the physical properties of the oxidizing species and the structure of the oxide. Figure 2, which is an Arrhenius plot of the oxidation rates (derived from Fig. 1) shows that indeed, the above equation describes the oxidation process well and enables us to determine K_0 and E_q.

Preliminary measurements yield dielectric strengths of 2.10×10^6 V cm^{-1} and a pinhole density of about 100 cm^{-2} for a 4700-Å-thick $NiSi_2$ sample with 1200-Å SiO_2. A pinhole was defined in this measurement as a localized defect which reduces the dielectric strength. Both values are compatible with integrated circuit requirements. Note that the pinhole density is for an oxide grown in a standard laboratory that is not equipped with special atmospheric control.

This initial study establishes the feasibility of using $NiSi_2$ as metal gate and interconnect in integrated circuit technology and characterizes the rates of the oxidation process. Other aspects, left open, that should be investigated further before practical implementation are the properties of a metal/SiO_2/ silicon structure with $NiSi_2$ gate metallization, resistance to electromigration, capability to be defined into fine patterns, and chemical compatibility to integrated circuit processing; but out initial results look promising.

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TABLE I. Oxidation characteristics of different silicides compared to that of silicon.

Temperature range (°C)			Si (Ref. 12) 700–1200	$NiSi_2$ 700–900	$TiSi_2$ (Ref. 15) 900–1050	$TaSi_2$ (Ref. 18) 900–1050	WSi_2 (Ref. 22) 1000–1200
Activation energy (eV)	Dry	linear	2.0	···	no oxidation	no oxidation; oxidation[19]	no oxidation
		parabolic	1.24	1.5			
	Wet	linear	2.0	···	2.0	···	···
		parabolic	0.71	1.0	1.4	1.4	1.0[a]
Oxide thickness (Å) 1 h at 900 °C-wet			2000	2700	2200	1200	2900[b]

[a] WSi_2 oxidation goes as $x^n \propto t$, where x is the oxide thickness, t is time, and n was found[22] to be 1.8.
[b] Extrapolated; error is about $\pm$ 15%.

We found that the growth is controlled by the SiO_2 (bulk and/or surfaces) and not by the silicide. The parabolic growth rate implies a diffusion-limited process. From oxidation studies of Si, it is known that the diffusing species through the oxide[9–11] is oxygen (or oxygen-containing molecules). Since SiO_2 grows in our case too, we infer that the rate-limiting process is transport through the oxide, and that some oxygen-containing molecules are the moving species.

The oxidation kinetics of Si[12,13] is described by a combination of linear and a parabolic rate constants. In Fig. 3, we compare the silicon dry oxidation data[12] with that the $NiSi_2$. Clearly, the oxidation rate of $NiSi_2$ is higher due to the absence of a surface kinetics limitation (no linear regime). If there is an initial region where $NiSi_2$ oxidation obeys a linear time dependence, the corresponding SiO_2 thickness must be much smaller than that of the Si oxidation case. Furthermore, the parabolic rate constant for Si dry oxidation has an activation energy of 1.24 eV,[12] but that of $NiSi_2$ is 1.5 eV (see Table I). These differences and those observed also for wet oxidation (see Table I) suggest that the details of the diffusion may differ between Si and $NiSi_2$. Recent and detailed experimental investigations have established, however, that the dry oxidation of Si has a non-Arrhenius behavior and does not obey the linear-parabolic oxidation model exactly, so that the interpretation of activation energy values and their differences is not straightforward.[14]

It is of interest to compare the oxidation of $NiSi_2$ to that of other silicides. Such studies have been performed on $TiSi_2$,[15,16] $HfSi_2$,[17] $TaSi_2$,[18,19] $MoSi_2$,[20] WSi_2,[21] $CoSi_2$,[10] and PtSi.[10] Except for $HfSi_2$, all these silicides form an SiO_2 layer on top of the silicide under the appropriate oxidation conditions. It is reported that $TiSi_2$,[16] $TaSi_2$,[18] and WSi_2[22] do not oxidize in dry oxygen environment even at temperatures of 1000 °C and above. A contradictory report states that $TaSi_2$ (Ref. 19) can be dry oxidized. In the $TiSi_2$ and $TaSi_2$ cases, metal oxides TiO_x and Ta_2O_5 were formed on top of the SiO_2. $CoSi_2$ was steam oxidized[10] only at one temperature and parabolic growth rate was established.

The only detailed kinetics analysis reported is for Ti, Ta, and W disilicides. The results are summarized in Table I. We cannot explain the differences in the oxidation kinetics for the above silicides. It is apparent that $NiSi_2$ oxidation is not similar to either Si oxidation or the Refractory metal silicides. We think that the diffusion species through the SiO_2 is likely to be the same in all cases. The observed differences then may reflect structural variations of the growing SiO_2 layer and/or additional diffusion processes for some silicides. As pointed out by Pliskin[23] stress also can affect the oxide rate. To fully understand the oxidation process, further investigations are needed.

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