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INTERMETALLIC REACTIONS IN VACUUM-DEPOSITED  
NICKEL AND GOLD FILMS ON (111) SILICON SINGLE CRYSTALS\*

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Pure nickel and gold thin films were vacuum-deposited on (111) silicon single crystals. When Ni/Au/Si or Au/Ni/Si samples were heated to about 550°C in situ, hexagonal or deformed hexagonal shaped crystallites were formed on the silicon substrates. The composition of these crystallites was determined by using x-ray diffraction, scanning electron microscopy and scanning Auger microprobe methods. The crystallites were identified as NiSi<sub>2</sub>. The crystallites on the (111) silicon plane parallel to the surface appeared as regular hexagons while the inclined crystallites resembled trapezia. The results of Auger spectra and in-depth composition profiles for Ni, Au, and Si showed that the NiSi<sub>2</sub> crystallites are islands in a matrix of Au-Si eutectic.

Key words: thin films, intermetallics, silicide formation

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### Introduction

It is known that silicide-forming transition metal films react with silicon substrates at temperatures well below the eutectic or peritectic temperatures (1-3). Lowered reaction temperatures have been associated with enhanced interdiffusion at the film-substrate interface (4). A number of factors that can cause enhanced interdiffusion have been discussed by Balluffi and Blakely (5).

During a mass spectrometric study of impurities associated with Au/Ni and Ni/Au films on silicon wafers, we found that crystallites of unknown composition were formed when the samples were heated in vacuum to about 550°C for about ten minutes. By combining x-ray diffraction, electron stimulated x-ray fluorescence, and in-depth Auger electron spectrometry, we determined that the crystallites were NiSi<sub>2</sub>. In the absence of Au, Sundstrom, et al. (2) and Tu, et al. (6) have found that at temperatures exceeding 750°C NiSi<sub>2</sub> is formed from the interaction of Ni films and Si substrates. Therefore, it appears that the presence of gold leads to a significant reduction in the temperature at which NiSi<sub>2</sub> can be formed.

### Experimental

Pure gold wire and nickel strip were separately evaporated from a resistively-heated U-shaped tungsten filament onto the unpolished (111) surface of n-type silicon wafers. The silicon substrates were P doped with resistivities of 50 ohm-cm. Ni/Au/Si samples were prepared by depositing gold on silicon substrates and then nickel upon the gold film. Au/Si and Au/Ni/Si samples were prepared in a similar fashion. Immediately before loading into the vacuum bell-jar for metal deposition, the silicon substrates were rinsed in cold distilled water, degreased in acetone and etched in a dilute hydrogen fluoride solution for 1 min. to reduce the oxide thickness on the silicon substrates. The background pressure during evaporation was kept below  $2 \times 10^{-5}$  torr. The substrate-to-source distance was approximately 5 cm. During deposition, the temperature of the silicon substrates never exceeded about 50°C. The substrate temperature was determined by a chromel-alumel thermocouple held against the substrate.

The thickness of the nickel and gold films were about 1100 Å and 2800 Å, respectively, as determined from Auger in-depth profiles.

The samples were heated in vacuum to about 550°C for approximately ten min. by electron bombardment. The background pressure during heating the samples was maintained below  $4 \times 10^{-7}$  torr. After heating, the samples cooled to room temperature within a few min.

The samples were then removed from the vacuum chamber and examined with a SEM. The surfaces of the samples showed microstructure similar to the Au-Si eutectic structure found by Hellawell (7) and Sinha (8) in bulk gold-silicon alloys.

Ni/Au/Si and Au/Ni/Si samples had other features after heating. These features had the form of crystallites, as shown in Fig. 1. The shape of the crystallites resembles a slightly deformed hexagon. This shape is seen more clearly in Fig. 2.

### X-Ray Diffraction Analysis

The crystallites formed on some samples were separated from the substrates by aqua regia. These crystallites were washed several times with distilled water to remove the residual gold solution. They were then dried in air, and examined by x-ray diffraction. Cerac\* NiSi<sub>2</sub> powder was used for comparison with the crystallites.

Debye-Scherrer powder patterns were obtained using CuK<sub>α</sub> radiation and a Ni filter. Some of the many lines on the sample pattern could be attributed to diffraction by pure gold. The diffraction lines of gold decreased in intensity with increased washing time. No shift in the positions of the gold lines occurred as a result of this treatment. This suggests that gold was not involved as a part of the crystallites. Auger electron analysis later confirmed this. The remainder of the samples lines were indexed as NiSi<sub>2</sub> which has a cubic calcium fluoride (C1)

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\*Cerac/Pure, Inc., Menomonee Falls, Wisconsin

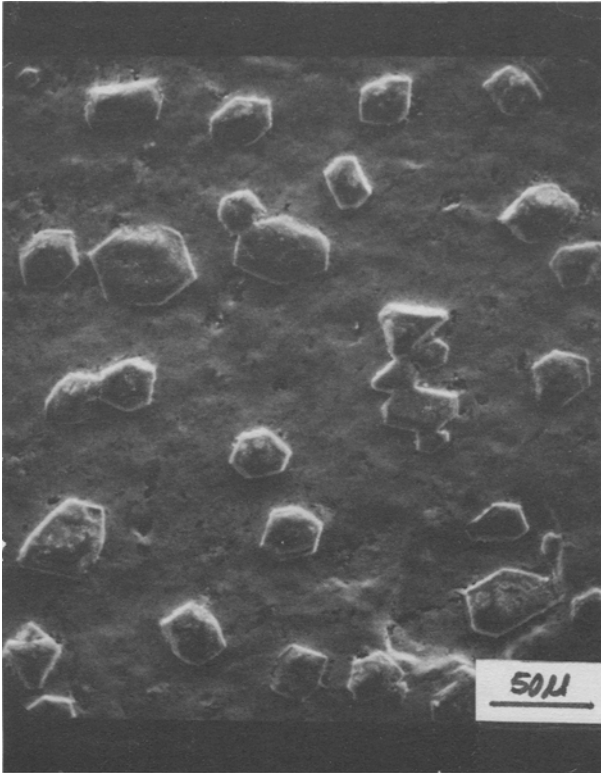


Fig. 1. SEM photograph of the crystallites in the Ni/Au/Si sample. The crystallites are  $\text{NiSi}_2$ .

structure (3,9-11). Table 1 lists the observed diffraction lines together with the calculated relative integrated intensities. The calculated lines for  $\text{NiSi}_2$  could be accounted for except those lines whose intensities were so low as not to be visible on the x-ray film even after prolonged exposure.

It should be noted that  $\text{NiSi}_2$  with a lattice parameter of 5.406 Å represents a good match with the diamond structure of Si with a lattice parameter of 5.4301 Å.

Table 1. Comparison of the Calculated Relative Integrated Intensities and Observed Intensities for NiSi<sub>2</sub> (a = 5.406 Å, CaF<sub>2</sub>(Cl) Structure)

hkl	$\theta$	$d(\text{\AA})$		I	I/I <sub>1</sub>	$d(\text{\AA})$		Observed Intensity
		Calculated	"Cerac"NiSi <sub>2</sub>			Observed	Observed Intensity	
111	14.317	3.115	3.118	1928479	80	3.119	S	
200	16.557	2.703	*	8064	<1	*	*	
220	23.766	1.911	1.913	2420449	100	1.916	S	
311	28.203	1.630	1.631	738672	31	1.632	W	
222	29.575	1.561	*	372	<1	*	*	
400	34.745	1.351	1.352	345438	14	1.354	VW	
331	38.393	1.240	1.241	282595	12	1.243	VW	
420	39.583	1.209	*	136	<1	*	*	
422	44.268	1.103	1.105	720499	30	1.105	W	
511	47.760	1.040	1.042	179627	7	1.045	VW	
440	53.706	0.957	0.959	315609	13	0.960	VW	
531	57.450	0.9138	0.9140	340110	14	0.9143	VW	
600	58.747	0.9010	*	184	<1	*	*	
620	64.307	0.8547	0.8548	728639	30	0.8550	VW	
533	69.117	0.8244	0.8247	203402	8	0.8250	VW	

\* not observed S: strong; W: weak; VW: very weak I<sub>1</sub> = 24204.49

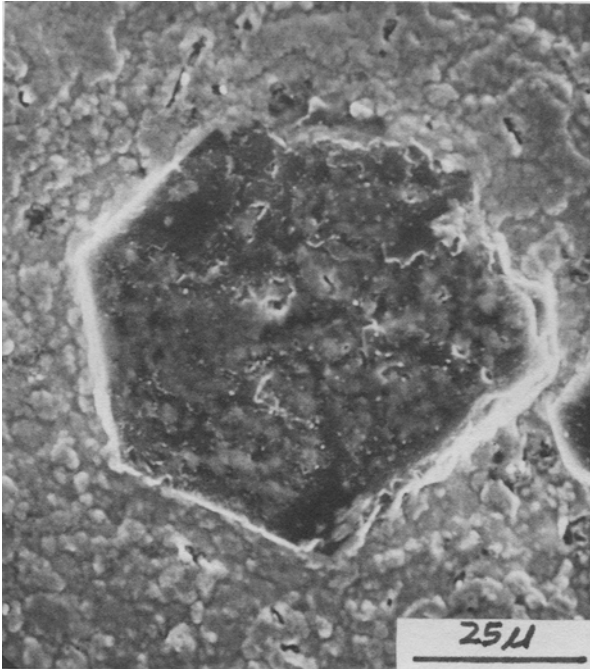


Fig. 2. SEM photograph of the microstructure associated with the Au-Si eutectic in the Au/Ni/Si sample. Au (light area) was recrystallized from the liquid Au-Si eutectic.

### Auger Electron Analysis

Inert gas ion sputtering combined with Auger electron spectroscopy was shown by Palmberg (12) to be useful for in-depth composition analysis of materials. This method has been applied to many studies of compound formation, including the growth of  $\text{Ni}_2\text{Si}$  on silicon (13). Here, in-depth Auger electron spectroscopy was used to determine the composition of the matrix material surrounding the crystallites as well as the crystallites themselves. To distinguish between the two regions, it was necessary

to use a narrow (5  $\mu\text{m}$ ) electron beam to generate the Auger electrons. Our instrument has this capability.\*

Fig. 3 shows an in-depth composition profile for the same surface matrix as in Fig. 2. The region appears to be a gold-silicon alloy about 1500  $\text{\AA}$  thick. Nickel is not detected in either the Au-Si alloy or in the region below it.

Fig. 4 shows the profile for a crystallite similar to that shown in Fig. 2. Although some gold is present in a layer about 1200  $\text{\AA}$  thick, the main constituents of the crystallite are nickel and silicon. Beyond 5100  $\text{\AA}$ , the silicon intensity increases while the nickel signal decreases, thus indicating the presence of an interface. The profile analysis shows that thickness of the crystallites is significantly larger than the thickness of the surrounding matrix. The ratio of the silicon 92 eV to the

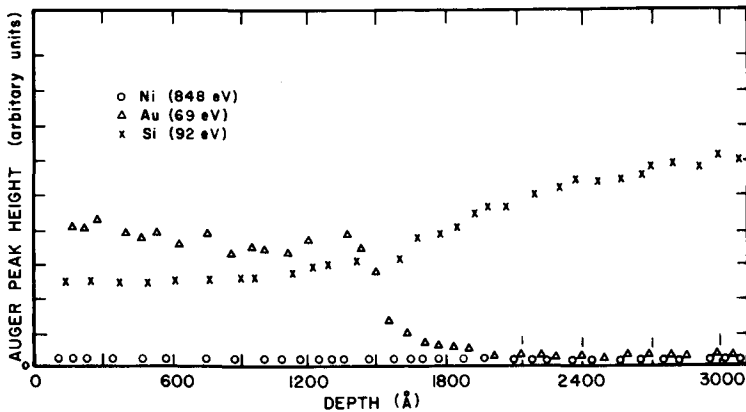


Fig. 3. In-depth composition profile for Ni, Au, and Si of the surface matrix of a Ni/Au/Si sample heated to 550°C for 10 minutes.

\*Model 545, Physical Electronics Industries, Eden Prairie, Minnesota



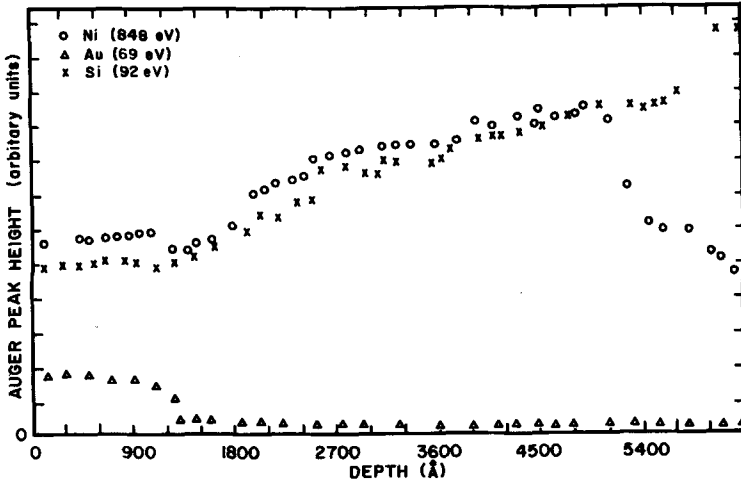


Fig. 4. In-depth composition profile for Ni, Au and Si of the crystallites of a Ni/Au/Si sample heated to 550°C for 10 minutes.

nickel 848 eV Auger peak heights for the crystallites is consistent with the same ratio measured for Cerac\* NiSi<sub>2</sub>.

#### Non-Dispersive X-ray Analysis

The Auger in-depth composition profiles of crystallites showed that they contained gold to a depth of over 1000 Å. Therefore, in order to study the gold-free region with non-dispersive x-ray analysis, the gold containing layer was removed by ion sputtering. The sputter-etched crystallites were then examined in SEM. An Ortec non-dispersive x-ray unit was used to obtain a chemical analysis of the crystallites. Since x-ray diffraction of the separated crystallites had shown them to be NiSi<sub>2</sub>, a sample of Cerac\* NiSi<sub>2</sub> was used in the SEM unit for comparison purposes. Separated crystallites were also examined in the SEM unit.

\*Cerac/Pure, Inc., Menomonee Falls, Wisconsin

The peak heights, which are proportional to the number of x-ray pulses, recorded by the Ortec non-dispersive x-ray unit, are shown in Table 2. For all samples examined, the ratio of the silicon and nickel x-ray counts is two to one. For the crystallites alone, this fact does not prove that their composition is  $\text{NiSi}_2$ , since the instrument may not have the same sensitivity for each element. However, the fact that the same ratio is obtained for a sample of known composition does support the conclusion that the crystallites are indeed composed of  $\text{NiSi}_2$ .

#### Mechanism of the Formation of $\text{NiSi}_2$

In the Ni/Au/Si sample, it is likely that the gold film reacted with the silicon substrate as the temperature increased over the Au-Si eutectic temperature ( $370^\circ\text{C}$ ). Both nickel and silicon atoms could easily migrate into the eutectic and react to form  $\text{NiSi}_2$ . In the Au/Ni/Si sample, it is probable that gold diffused through pinhole type defects and grain boundaries of the nickel film to the Ni/Si interface. The gold and silicon then reacted to form the Au-Si eutectic. This liquid eutectic probably acted again as a high diffusivity medium for nickel and silicon atoms which then reacted to form  $\text{NiSi}_2$ . In both cases, gold might have been separated from the Au-Si eutectic when the silicon in the eutectic reacted with nickel and some of the Au-Si eutectic might have remained on the surface.

The unit cells of both Si and  $\text{NiSi}_2$  contain eight silicon atoms so that only a short range movement of the silicon atoms would be required for precipitation of the long range diffusing interstitial nickel atoms. From the similarity of structures and lattice parameters of both Si and  $\text{NiSi}_2$ , epitaxial growth of the  $\text{NiSi}_2$  on the silicon substrate can be expected (4). Indeed, it seems that the hexagonal crystallites lie with their (111) plane parallel to the (111) silicon substrate surface. The  $\text{NiSi}_2$  crystallites which lie on the (111) substrate plane parallel to the surface appear as regular hexagons, while the inclined crystallites resemble trapezia.

Table 2. List of Peaks Height and Intensity Ratio of Si and Ni in the Crystallites on the Surface of the Sample, the Crystallites Separated from the Sample and Cerac\* NiSi<sub>2</sub> Taken by the SEM X-Ray Analyzer

Sample	Si Peak	Ni Height(cm)	Si/Ni Intensity Ratio
Crystallites on the Sample	3.2	1.6	2
Crystallites Separated from the Sample	1.0	0.5	2
Cerac* NiSi <sub>2</sub>	4.0	2.0	2

\*Cerac/Pure, Inc., Menomonee Falls, Wisconsin

### Conclusion

NiSi<sub>2</sub> crystallites are formed when Ni/Au/Si and Au/Ni/Si thin film samples are heated to 550°C. They appear to be formed by the rapid diffusion of Ni and Si in an Au-Si eutectic which forms at the Si surface. The orientation of the crystallites indicates they grow epitaxially at the (111) silicon surface. The nickel originally present as a thin film is incorporated into the crystallites. After formation, the crystallites are surrounded by an Au-Si matrix. Evidently, in the presence of a gold-silicon eutectic, NiSi<sub>2</sub> crystals can grow at temperatures 200° lower than when gold is absent.

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