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DIFFUSION OF NICKEL IN SILICON BELOW 475 °C

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Nickel films were deposited on (100) and (111) surfaces of single-crystal silicon and were then annealed. The conditions under which the nickel is deposited determine whether or not a Ni–Si compound forms on annealing. It is postulated that defects are necessary for the formation of a Ni–Si compound at annealing temperatures below at least 475 °C, although the presence of defects may not necessarily cause the formation of a silicide. For substrate temperatures below 70 °C, defects are created during the vapor deposition of nickel on silicon. These defects always result in the formation of nickel silicide when the sample is annealed at higher temperatures. When nickel is deposited on defect-free silicon at temperatures of about 250 °C no defects are generated and, although interdiffusion of nickel and silicon occurs, silicide formation does not take place upon subsequent annealing below 475 °C. The activation energies for the diffusion of nickel into (100) silicon and (111) silicon were determined.

1. INTRODUCTION

The formation of a silicide between silicon and certain metals such as nickel, palladium and platinum at annealing temperatures above 200 °C is well known^{1–9}. Various analytical methods have been used for these studies, such as helium ion backscattering^{1,3–6}, Auger electron spectroscopy^{1,10} and Seemann–Bohlin X-ray diffraction¹. The Ni–Si binary system has six stable intermetallic phases¹ below 950 °C. The Ni₂Si phase has been found to exist in samples heat treated in the range 200–350 °C. After annealing for 1 h at 350 °C, Ni₂Si has been detected together with a small amount of NiSi. NiSi is stable below 700 °C. However, it has also been reported¹⁰ that nickel films on the (100) surface of single-crystal silicon diffuse into the substrate without forming a silicide when annealed between 250 and 350 °C. It was the object of this study to determine the conditions under which a silicide will or will not form during annealing.

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2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

The following sets of samples were used.

2.1.1. Group A

These were (100) silicon and (111) silicon single-crystal samples (Monsanto Corporation, St. Louis, Missouri, U.S.A.) (p doped; resistivity, $10\ \Omega\ \text{cm}$) covered with about $4500\ \text{\AA}$ of nickel. The silicon surface was polished and chemically cleaned before the nickel deposition, which was performed by r.f. sputtering for about 10 min. During the deposition the temperature rose to about 250°C .

2.1.2. Group B

These samples were prepared with the following conditions. A nickel evaporator was constructed which consisted of a tungsten wire around which a fine nickel ribbon of 99.99% purity was wrapped. The evaporation rate could be controlled by altering the current through the tungsten wire. The substrates used were (100) silicon and (111) silicon. The pressure was in the 2×10^{-7} Pa region before deposition and was about 1×10^{-6} Pa during the deposition. The following conditions were varied: (a) the substrate temperature (between 70 and 350°C during deposition); (b) the substrate crystal (resistivities of 10 and $1000\ \Omega\ \text{cm}$); (c) the cleaning techniques for the substrate surface; (d) the deposition rate; (e) the film thickness.

2.2. Heat treatment

The Ni/Si samples were heated in a small oven. A constant flow of high purity argon was maintained in the oven throughout the heat treatment to prevent oxidation. Some of the group B samples were heated in the vacuum. The substrate temperature for both group A and group B samples was measured with a chromel–alumel thermocouple. Different annealing temperatures and times were chosen for different samples according to the purpose of the investigation. The highest annealing temperature was 475°C and the longest annealing time 48 h.

2.3. Depth profiles

The samples were mounted on a rotatable sample holder in a scanning Auger microprobe (SAM) bell-jar (Physical Electronics Industries, Inc., Edina, Minnesota, U.S.A.). Selected Auger electron peak amplitudes were recorded by multiplexing peaks during sputtering. In order to sputter the samples the bell-jar was filled with argon to a pressure of 6.7×10^{-3} Pa. The sputter beam energy was $2\ \text{keV}$. For Auger analysis the electron beam energy was $4\ \text{keV}$, the beam diameter about $5\ \mu\text{m}$ and the beam current about $10\ \mu\text{A}$. The sputter rate for nickel was calculated as $29 \pm 3\ \text{\AA}\ \text{min}^{-1}$ by measuring the time required to sputter etch through several nickel films of known thickness. The thickness of the calibration films was determined with a quartz crystal microbalance.

3. RESULTS AND DISCUSSION

3.1. Group A samples

Figure 1 shows a typical depth profile (silicon (92 eV) and nickel (61 eV)) for an

unannealed sample of nickel on (111) silicon. Although it is not shown in Fig. 1, oxygen ($1 \times$) was also plotted. However, the oxygen peak was not detected throughout the profile. The initial depth of penetration of nickel into silicon appears to be about 1400 Å. Part of this apparent initial penetration depth may have been caused by ion sputtering effects¹¹ but most of it was due to sample heating during the r.f. sputter deposition of nickel when the sample was heated to about 250 °C. For room temperature deposition the initial penetration depth is only about 400 Å.

Figure 2 shows a typical depth profile for an annealed sample. In this case the sample was annealed at 375 °C for 4.5 h. Again, the O (510 eV) ($1 \times$) peak could not be detected at any point in the profile. However, when the sputter process was stopped, at different stages, a very small amount of oxygen was detected at the interface, with a larger amount at the nickel side of the interface. These observations may be explained as follows. It is postulated that the oxygen is supplied by the residual gas in the bell-jar and leads to the oxidation of the nickel. The oxidation of nickel is considerably stimulated by the electron beam¹². Since the presence of nickel favors oxide formation, the oxygen concentration will follow the nickel concentration and will be higher on the nickel side of the interface. This also explains why oxygen is observed in the Auger scans but not in the depth profiles. No other impurities were detected.

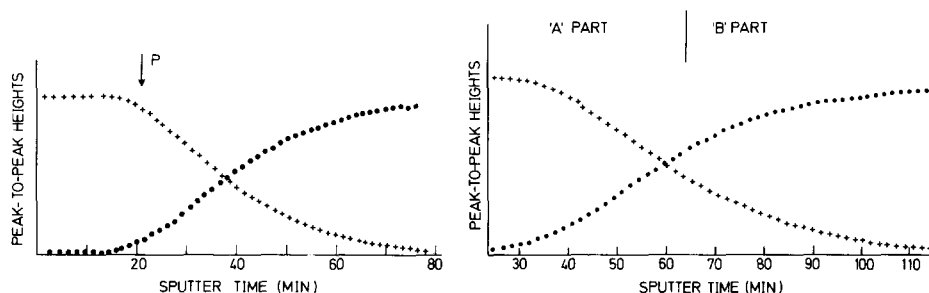


Fig. 1. A depth diffusion profile for nickel and silicon before heat treatment for r.f. ion-sputtered nickel on (111) silicon: sputter rate, 29 Å min^{-1} ; +, nickel (61 eV), $2 \times$; ●, silicon (92 eV), $1 \times$.

Fig. 2. A depth diffusion profile for nickel and silicon after annealing at 375 °C for 4.5 h for r.f. ion-sputtered nickel on (111) silicon: sputter rate, 29 Å min^{-1} ; +, nickel (61 eV), $2 \times$; ●, silicon (92 eV), $1 \times$.

The nickel concentration percentage was plotted against sputter time on probability paper for these profiles. The "A" and "B" sections in Fig. 2 define the ranges of concentration over which the probability plot (Fig. 3) gives two linear segments. The method used to calculate the diffusion coefficient D is that outlined by Hall and Morabito¹³. Figure 4 shows a plot of $\ln D$ versus T^{-1} for both the "A" and "B" parts. From the slope of the lines the activation energy E was determined by least-squares fit as 1.88 eV for the "A" part and as 1.22 eV for the "B" part with an uncertainty of $\pm 20\%$. D_0 is the pre-exponential factor in the equation $D = D_0 \exp(-E/kT)$ and is of the order of 10^{-1} and $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the "A" and "B" parts respectively.

The lattice diffusion coefficient of nickel in silicon has been measured by Bonzel²⁴ to be $0.1 \exp(-1.9 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$ in the temperature range 450–800 °C.

The present calculated values for the activation energy and D_0 for the "A" part agree with those of Bonzel. Bonzel has proposed the dissociated substitutional interstitial diffusion mechanism for the diffusion of nickel in silicon. This mechanism is therefore assumed to apply to the "A" part. For the "B" part the activation energy is lower and the diffusion coefficient higher. This suggests that the contribution of interstitial nickel is more important in this part, resulting in a more rapid movement of the nickel, leading to deeper penetration.

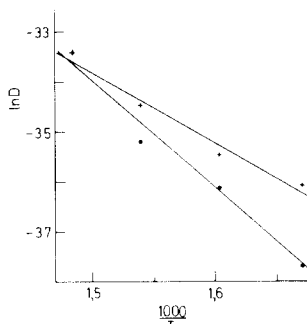
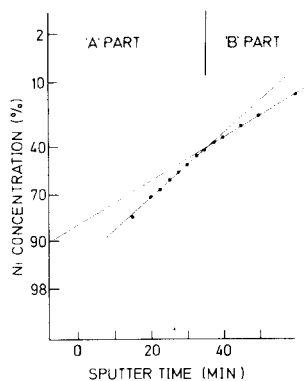


Fig. 3. A probability plot of the Ni/Si data for a sample annealed at 350 °C for 4 h.

Fig. 4. A plot of $\ln D$ vs. reciprocal absolute temperature for nickel on (111) silicon: ●, "A" part; +, "B" part.

For nickel on (100) silicon, plots similar to those in Figs. 1 and 2 were obtained, although the interface for the unannealed sample was thinner¹⁰. For (100) silicon the activation energy for the "A" part was calculated to be 0.28 eV and for the "B" part to be 0.26 eV with an uncertainty of $\pm 20\%$. D_0 was of the order of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$. These values for (100) silicon appear to be much too small in comparison with that of (111) silicon and other published values for similar substances, but no explanation of this can be offered at this stage.

Hence, there is quite a difference in the activation energies for the two different substrates. Another difference is the following. The annealing temperatures for the nickel on (111) silicon samples were in the range 325–400 °C. For 300 °C and below no diffusion was detected. A diffusion coefficient for nickel in (100) silicon was measurable for annealing at 250 °C. Therefore the nickel on (100) silicon samples were annealed between 250 °C and 350 °C. Although these differences were noted, no detailed explanation is offered here, except to suggest that they might be due to directional differences in the atomic arrangement normal to the substrates for the first few atom layers.

When we performed the vapor deposition of nickel onto (100) silicon or onto (111) silicon at room temperature there was always a plateau in the depth profile after annealing (Fig. 5). This plateau indicates that a silicide layer was formed between the nickel and silicon, as has also been reported elsewhere^{1–5}.

For the group A samples no plateau was formed even after heat treatment at 475 °C for 55 min (Fig. 6). From the absence of the plateau it can be inferred that in this case no silicide layer was formed.

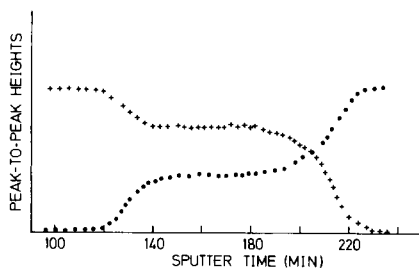


Fig. 5. A typical in-depth diffusion profile for nickel and silicon after annealing for nickel evaporated onto silicon at room temperature: sputter rate, 29 \AA min^{-1} ; +, nickel (61 eV), $2 \times$; •, silicon (92 eV), $1 \times$.

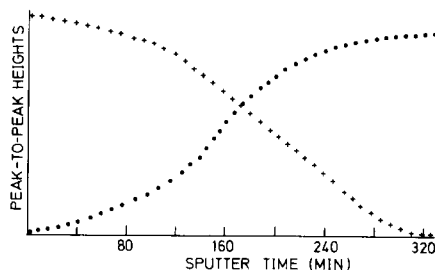


Fig. 6. A depth diffusion profile for nickel and silicon after annealing at 475°C for 55 min for r.f. ion-sputtered nickel on (100) silicon: sputter rate, 29 \AA min^{-1} ; +, nickel (61 eV), $2 \times$; •, silicon (92 eV), $1 \times$.

3.2. Group B samples

We tested the different group B samples to find out which of the parameters (a)–(d) (Section 2.1) influence the formation of silicide. It was found that only the technique of preparing the substrate surface and the temperature of the surface during deposition had an appreciable influence, the temperature having the greatest influence. For the substrate at room temperature (a maximum of 70°C during the deposition) a very well-defined plateau indicates silicide formation after annealing. For higher deposition temperatures this plateau becomes less well defined. For a deposition temperature of 250°C a depth profile like that in Fig. 2 was obtained after annealing. This profile was not always reproducible in that sometimes there was a little bend in the curve showing the start of a plateau. At different points on the surface of the same sample this small plateau was of different lengths. When the substrate was cleaned by sputtering or by heating to 1200°C and deposition took place with the substrate at 250°C , a small plateau was more likely to form after annealing than when the substrate was cleaned finally only by chemicals.

For the resistive evaporation of nickel onto silicon at 250°C for 10 min with no further annealing, the profile looks much the same as that in Fig. 1. A marker experiment was performed by simply not cleaning the surface before deposition. A distinct oxygen maximum was detected at position P, Fig. 1, before and after annealing, indicating the position of the original interface. (We used this technique because when we applied it to the case of room temperature deposition, in which case a silicide was formed, the oxygen appeared between the nickel and the silicide, *i.e.* at the same position as the xenon in a xenon-implanted marker experiment¹.) The marker experiment indicated that during the deposition at 250°C and subsequent annealing nickel was the faster diffusing species. It also showed that oxygen at the surface does not prevent the formation of silicides when nickel is present. The next step was to use preferential etching to delineate defects on the substrate. The nickel film on the samples subjected to this investigation was first polished off chemically. Then the standard Secco¹⁴ etch was used. The following results were obtained.

3.2.1.

The group A sputter-deposited samples, *i.e.* the samples which give no silicide formation, show a flat featureless surface after etching (Fig. 7). This result was obtained for samples before deposition, after deposition and after annealing.

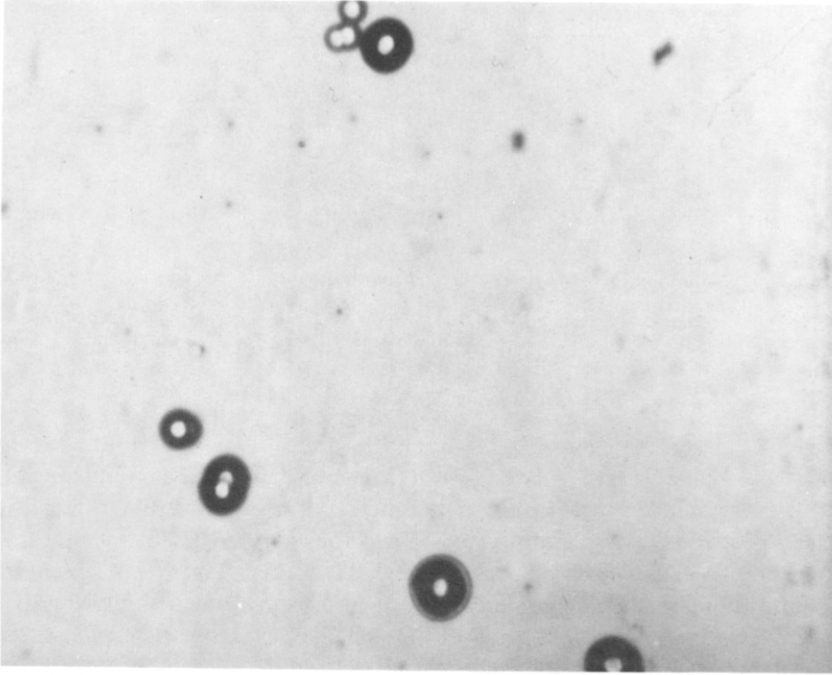


Fig. 8. A photomicrograph of a region of the sample described in the Section 3.2.3. Magnification 500 \times .

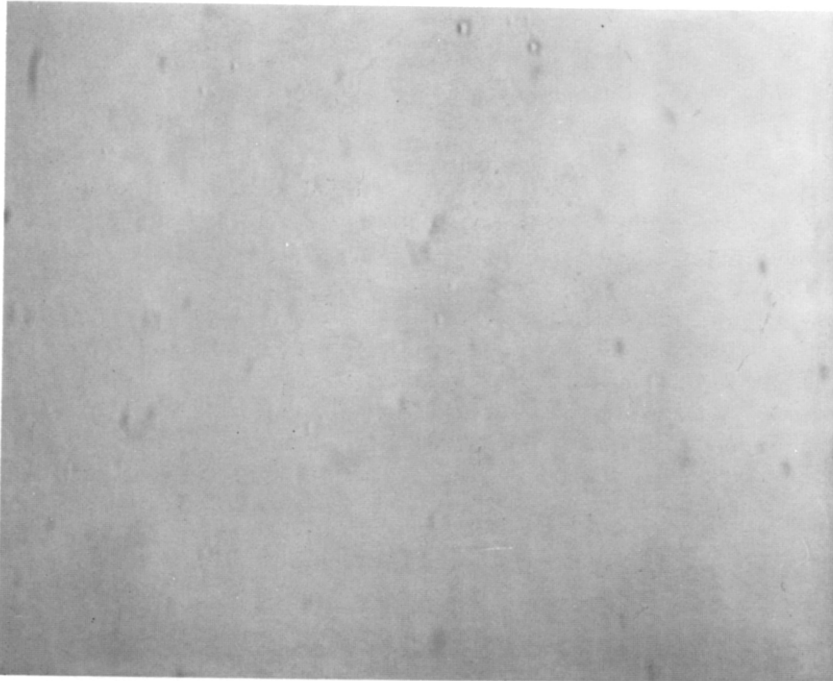


Fig. 7. A photomicrograph of a region of the sample described in Sections 3.2.1 and 3.2.2. Magnification 500 \times .

3.2.2.

The substrates were prepared in the same way as in 3.2.1 but the nickel was deposited by means of resistive evaporation for the substrate at 250 °C. After etching, the surface looks the same as that in Fig. 7 both before and after annealing. These samples also do not show silicide formation after annealing.

3.2.3.

The samples were prepared in the same way as in 3.2.2 but with a maximum temperature of 70 °C during deposition. In this case a plateau in the depth profile indicates the formation of a silicide during annealing. Figure 8 shows the defects as revealed by the Secco etch. A similar result was obtained before and after annealing. According to the results of the Secco etch, the samples were defect free before deposition. From Fig. 8 it can be concluded that defects are created on the substrate during deposition when the substrate is below 70 °C. When the substrate is at 250 °C during deposition no defects are created. For the same deposition time of 10 min, depositions were performed by resistive evaporation onto (111) silicon as well as onto (100) silicon substrates for different substrate temperatures. The samples were then cooled immediately. The thickness of the Ni-Si interface as a function of substrate temperature during deposition is presented in Fig. 9. Above about 200 °C the thickness of the interface increases rapidly with temperature, much more rapidly than for a sample onto which a deposition is made at room temperature and which is then subjected to a heat treatment for 10 min. Furthermore the depth profiles appear to be "diffusion"-like. Therefore during the deposition at higher substrate temperatures the nickel penetrates relatively quickly into the silicon substrate without forming an Ni-Si compound.

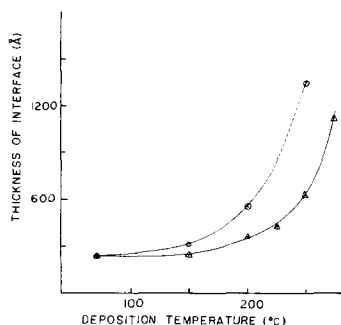


Fig. 9. A plot of interface thickness vs. temperature of the substrate during deposition: ○, Ni/Si (111); Δ, Ni/Si (100).

After room temperature deposition of 15 monolayers of nickel the 92 eV silicon Auger peak-to-peak amplitude was still about 7% of the amplitude just before deposition. This is strong evidence for cluster or island formation¹⁵. The stresses which accompany cluster formation could be the cause of the defects observed after deposition. Although the temperature of 250 °C during deposition might be too low for nickel to spread out uniformly on the silicon surface, it might be high enough to reduce thin film stresses so as to prevent the formation of defects.

In all cases where a silicide was formed during annealing, defects in the substrate were revealed by the Secco etch. We postulate here that defects are

necessary for the formation of an Ni-Si compound at annealing temperatures below at least 475 °C (the highest temperature we used).

The energy needed to remove a silicon atom from a low index smooth silicon surface is equal to a large fraction of the formation energy of a vacancy in silicon which is about 3.5 eV¹⁶ to 2.4 eV¹⁷. The silicide formation temperature is only about 0.3–0.4 of the melting points of silicon and the metals and is far below the eutectic temperature for their binary phase diagrams. Therefore, some mechanism must be responsible for the large reduction in the energy required to release silicon atoms from the silicon surface to sustain the silicide growth. Tu¹⁸ has suggested that the process that accomplishes this results from a mixing of silicon and metal atoms at the interface. However, the profiles in Figs. 1 and 6 show that although there was a mixing of nickel and silicon there was no silicide formation even after annealing at 475 °C.

Here mixing seems to be due to nickel that diffuses interstitially into silicon without weakening the covalent bonds enough to separate silicon atoms from the lattice at the surface. Where defects occur there will be dangling and unsaturated bonds of silicon atoms. These poorly bonded atoms do not require much energy to be released from the lattice to form an Ni-Si bond. The separation of one silicon atom exposes unsaturated bonds on other silicon atoms so that the process is kept going. At temperatures higher than 475 °C there might be enough thermal energy to break some silicon covalent bonds and to sustain the growth of nickel silicide.

3.2.4.

Another set of samples was prepared in the same way as in Sections 3.2.1 and 3.2.2 except that the silicon substrates had a resistivity of 1000 Ω cm. The Secco etch was also applied to some samples immediately after they had been finally prepared for deposition. Figure 10 shows the etch features caused by the Secco etch on these samples. Thus, even before deposition of nickel, the samples were not free of defects. The shapes of the etch features look different from those of the previous samples. These samples were also divided into two groups:

(a) samples in which the depositions were performed at a maximum substrate temperature of 70 °C and which were then annealed;

(b) samples in which the depositions were made at a substrate temperature of 250 °C and which were then annealed.

When the Secco etch was applied at any stage of the processes described in (a) and (b), etch features formed as in Fig. 10. We expected this because the surface was not defect free before deposition. As was mentioned earlier a “diffusion”-like profile was obtained for samples in (b), although in some cases a little bend in the profile indicates the start of silicide formation. That means that in some cases no silicide will form, although there are defects in the substrate. Although defects are necessary for the formation of an Ni-Si compound at annealing temperatures below 475 °C, the presence of defects will not necessarily cause the formation of a silicide. The type of defect structure appears to be important.

Wray and Prutton¹⁹ have reported that nickel is deposited epitaxially on (111) silicon when the substrate temperature exceeds 250 °C. The assumption that nickel grows epitaxially on both (111) silicon and (100) silicon when the substrate temperature exceeds 250 °C might serve as an explanation for the absence of a silicide layer in the group A samples after annealing²⁰. It can be argued that the

polycrystalline nickel atoms at the interface (deposited at room temperature) will be much more active chemically than epitaxially deposited nickel when the system is subsequently annealed at higher temperatures. However, there are two problems involved in such an explanation.

(i) According to Wray and Prutton the lowest temperature required for epitaxial growth is 250 °C. Thus, substrate temperatures considerably in excess of 250 °C during deposition which favor epitaxial growth will therefore inhibit the growth of silicide during subsequent annealing. However, we deposited six samples at substrate temperatures of 300 °C and higher (three at 300 °C, two at 325 °C and one at 350 °C) and only one (at 300 °C) showed no silicide formation upon subsequent annealing. At a substrate temperature of 250 °C during deposition, six out of a total of ten samples gave no silicide formation upon subsequent annealing.

(ii) It does not explain the gross migration of nickel into silicon without the formation of a silicide during annealing.

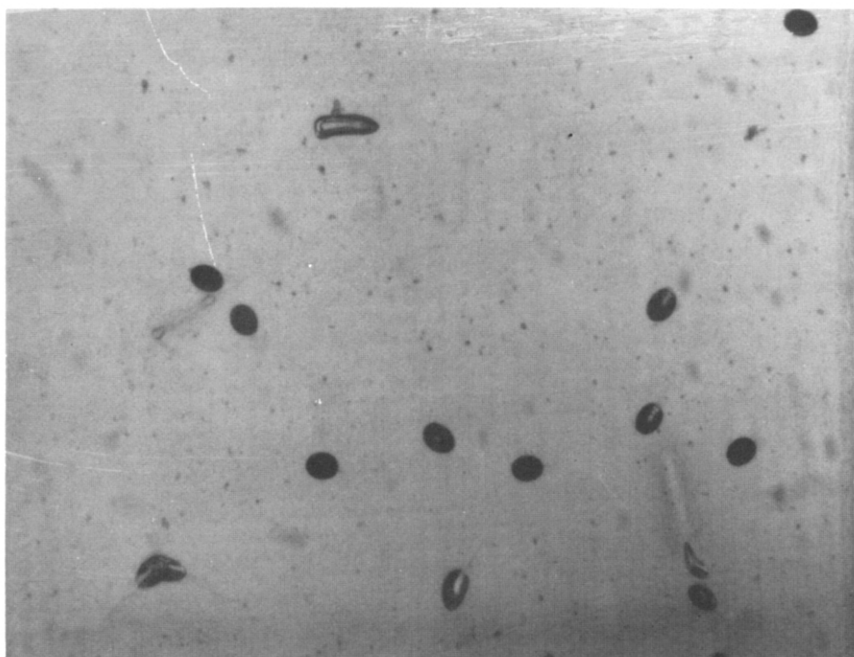


Fig. 10. A photomicrograph of a region of a sample described in Section 3.2.4. Magnification 500 \times .

The nickel concentrations as revealed by the diffusion profiles (e.g. Figs. 2 and 6) are much larger than those expected from the measured solubility of nickel in silicon²¹⁻²³. High concentrations of nickel in silicon could be due to the presence of defects but it has already been stated that no defects were observed in these samples. The answer to this discrepancy in the nickel concentration might be related to the deposition temperature however. The diffusion profiles mentioned were obtained only for samples on which the depositions were performed at elevated temperatures, whereas the depositions for the solubility measurements were all done at room temperature.

4. SUMMARIZING REMARKS

Nickel films were deposited on the (100) and (111) surfaces of single-crystal silicon and were annealed. To generate depth profiles, an SAM system was used. The conditions under which nickel was deposited were found to determine whether or not a Ni-Si compound forms during annealing. Of these conditions the substrate temperature appears to be the most important. The standard Secco etch was used to delineate defects on the substrate before and after deposition and after annealing.

When a deposition was made with the substrate at room temperature, there was always a plateau in the depth profile after annealing. Such a plateau indicates that a silicide layer has been formed. For these samples defects were revealed by the Secco etch after deposition, *i.e.* before annealing, even if the deposition was made on a defect-free substrate. Therefore the mere deposition of nickel introduces defects into the silicon substrate.

When nickel is deposited on defect-free silicon at a substrate temperature of about 250 °C, interdiffusion of nickel and silicon occurs but no defects are generated during the deposition. Upon subsequent annealing below 475 °C, further diffusion takes place without the formation of a silicide. In these samples the activation energies for the diffusion of nickel into (100) silicon and (111) silicon were determined as 0.27 and 1.5 eV respectively.

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