Interaction of metal layers with polycrystalline Si[†]

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Solid-phase reactions of metal films deposited on 0.5-μm-thick polycrystalline layers of Si grown by chemical vapor deposition at 640 °C were investigated by MeV ^{4}He backscattering spectrometry, glancing angle x-ray diffraction, and SEM observations. For the metals Al, Ag, and Au, which form simple eutectics, heat treatment at temperatures below the eutectic results in erosion of the poly-Si layer and growth of Si crystallites in the metal film. Crystallite formation is observed at $T \gtrsim 550$ °C for Ag, $T \gtrsim 400$ °C for Al, and $T \gtrsim 200$ °C for Au films. For the metals Pd, Ni, and Cr, heat treatment results in silicide formation. The same initial silicides (Pd_2Si, Ni_2Si, and $CrSi_2$), are formed at similar temperatures on single-crystal substrates.

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I. INTRODUCTION

In the application of polycrystalline silicon (poly Si) to integrated-circuit technology, metal layers, typically Al, are deposited on the poly Si and heat treated to provide electrical contacts. During this process it is desirable that the poly-Si layers maintain structural integrity. However, in a previous investigation[1] we observed that erosion of the poly-Si layer occurred, while at the same time Si crystallites grow in the Al film. Intermixing of the Al and Si occurred in the 400—560 °C temperature range, temperatures which lie below the eutectic value of 577 °C.

One of the purposes of the present study was to determine if this same phenomenon occurred in other metals which form simple eutectic systems with Si. In this respect, Au and Ag provide systems with eutectics below (Si-Au eutectic at 370 °C) and above (Si-Ag at 830 °C) that for the Si-Al system. Following heat treatment, the morphological changes in the poly-Si—metal structures were observed by scanning electron microscopy (SEM) and crystallites formation by glancing-angle x-ray diffraction.

The other objective of the study was to determine if crystallite growth occurred for metals which form silicides. For this aspect, metals were chosen which form silicides at the relatively low temperatures of 200—250 °C (Pd and Ni) and at the higher temperature of 450—550 °C (Cr) on single-crystal Si crystals.[2] The interaction of the poly Si with the metal films was studied by MeV $^4He^+$ backscattering. A second point of interest was to determine if the polycrystalline nature of the Si layer in contact with the metal film resulted in a change in the growth kinetics or the identity of the initial phases of the silicides as compared to those observed with single-crystal Si.

II. EXPERIMENTAL PROCEDURES

Polished single-crystal Si wafers of about 4-Ω cm n-type conductivity and oriented in ⟨100⟩ direction were thermally oxidized at 950 °C in steam to a thickness of 1000 ± 50 Å. The substrates thus obtained were covered with a layer of undoped poly Si formed at 640 °C by chemical vapor deposition. The polycrystalline nature of the deposited films was confirmed by the presence of Si rings in electron diffraction analysis, but no measurement of crystallite size was made. The thickness of this poly-Si film ranged from approximately 0.4—0.5 μm. Metal layers of Al, Ag, Au, Pd, Ni, and Cr were evaporated onto the unheated poly Si. Evaporation was performed by an electron gun for Al, Au, Pd, Ni, and Cr and by a Mo resistance heater for Ag. Vacuum pressure during evaporation was maintained below 5×10^{-7} Torr. Heat treatments were performed in vacuum at pressures below 10^{-7} Torr. All annealings were performed below the lowest eutectic temperature for each combination of metal and Si. A change in the morphology of the Si after heat treatment was monitored in the case of Al, Ag, and Au by scanning electron microcopy (SEM) after the metal layer was chemically removed with aqua regia for Al and Au and with HNO_3 for Ag. Elemental depth profiles for the sample were obtained by 2-MeV $^4He^+$ backscattering spectrometry. The glancing-angle x-ray diffraction technique (Read camera) was used for phase identification.

III. RESULTS

A. Simple eutectic systems

When an Al layer covers poly Si, the Si migrates into Al and forms crystalline precipitates within the Al during annealing below the Si-Al eutectic temperature (577 °C). The process of this recrystallization reaction can be observed with SEM by etching away the Al layer after annealing. The sequence of scanning electron micrographs in Fig. 1 shows the crystallization process of Si in Al as a function of time at 535 °C. In this sample the Al layer (1.2 μm) was much thicker than the poly Si (0.5 μm). The reaction begins with the formation of tiny crystallites at the interface between the Al layer and the poly-Si substrate [Fig. 1(a)]. With time, the crystallites grow bigger [Fig. 1(b)], and eventually all of the original poly-Si substrate is converted to distinct Si crystallites [Fig. 1(c)]. Beyond this point, some crystallites continue to grow at the expense of others [Fig. 1(d)]. However, the growth is confined to the lateral direction; the height of each

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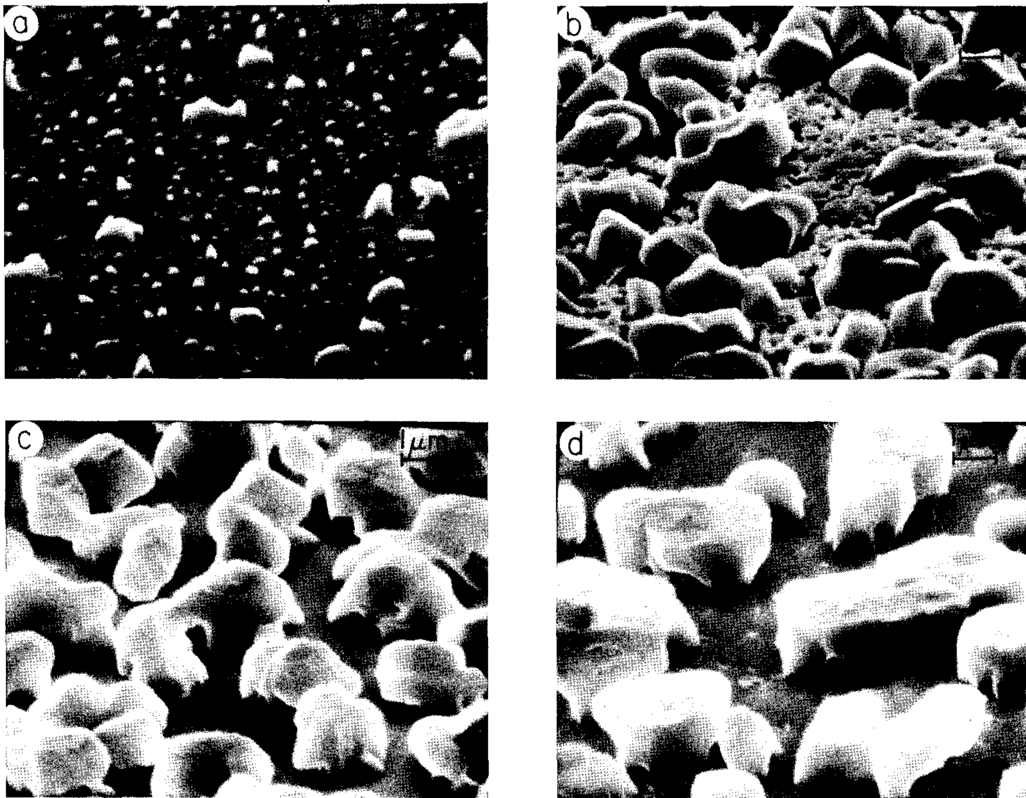

FIG. 1. Scanning electron micrographs of samples with 1.2-μm Al on 0.5-μm poly Si after annealing at 535 °C for (a) 1 min, (b) 5 min, (c) 1 h, and (d) 55 h. The Al was chemically removed before examination. The incident angle of the electron beam with respect to the normal of the sample is 60°.

crystallite is limited by the thickness of the Al layer. Similar dissolution of poly Si and formation of crystallites was observed at temperatures as low as 400 °C. However, at the lower temperatures the crystallites growth rate was substantially reduced. For example, the morphology of a sample heated at 400 °C for 30 min was similar to that shown in Fig. 1(b).

The crystal growth process of Si in Al can also be monitored by glancing-angle x-ray diffraction at each stage of the reaction. Before annealing, Debye-Scherrer rings are absent in x-ray diffraction pictures of the original poly-Si substrate which indicates that the grain size of the original poly-Si substrate is small and below the detection limit [Fig. 2(a)]. After annealing, Debye-Scherrer rings of Si appear, confirming the presence of Si crystallites [Fig. 2(b)]. Observation of the patterns reveals that each diffraction line consists of a multitude of individually resolved spots. This multispot feature of each diffraction line becomes more perceptible after long annealing [Fig. 2(b)], proving that the Si crystallites grow bigger with time.

A similar recrystallization is also observed when a Ag or Au layer is in contact with poly Si (see Fig. 3). The reaction can occur at temperatures as low as 550 °C for the poly-Si–Ag system and 200 °C for poly-Si–Au system. The corresponding eutectic temperatures are 830 °C for Si-Ag and 370 °C for Si-Au, respectively. X-ray diffraction analysis of these samples shows the presence of Debye-Scherrer rings corresponding to Si. The difference in the shape of the crystallites in Figs. 3(a) and 3(b) is due to the fact that the Ag layer was thin enough to geometrically confine the growth, while the thicker Au layer did not.

B. Silicide forming systems

To investigate the behavior of poly Si in contact with silicide-forming metals such as Pd, Ni, and Cr, the

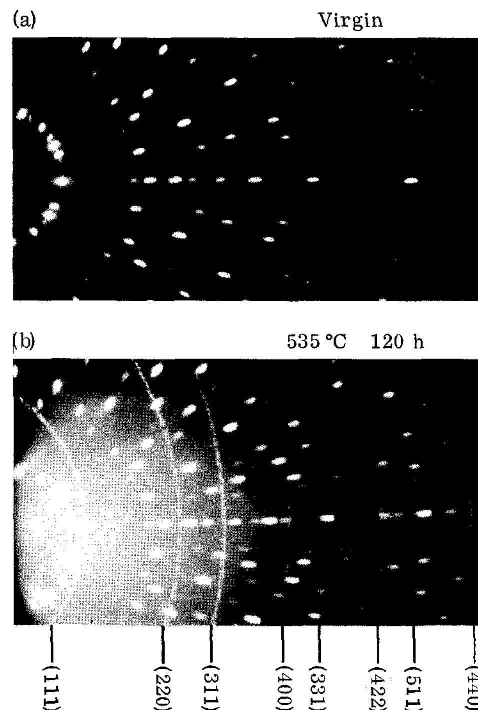

FIG. 2. X-ray diffraction patterns obtained from (a) 0.5-μm poly Si as-deposited on SiO_2 and (b) 1.2-μm Al on 0.5-μm poly Si annealed at 535 °C for 120 h. In (a) the spot pattern is due to the single-crystal Si substrate. Poly Si does not give rise to diffraction because of its very small grain size. In (b) the ring pattern is due to small Si crystallites. The Al was removed before exposing the sample to the x-rays.

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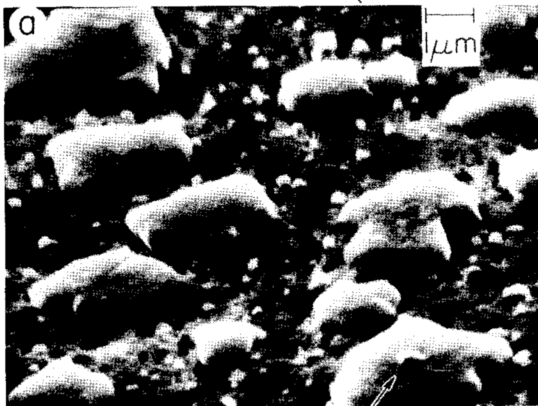

poly-Si—Ag

Regrown Si

poly-Si—Au

FIG. 3. Scanning electron micrographs of samples with (a) 0.7-μm Ag on 0.5-μm poly Si annealed at 600 °C for 15 h and (b) 1.5-μm Au on 0.5-μm poly Si annealed at 250 °C for 48 h. The Ag and Au were chemically etched by HNO_3 and aqua regia, respectively, before examination. The incident angle of the electron beam with respect to the normal of the sample is 60°.

samples were first annealed at temperatures where a silicide was known to form between these metals and a single-crystal substrate, i.e., 200—325 °C for Pd and Ni, and 450—500 °C for Cr. Figure 4 shows the backscattering spectra of a sample with 3700 Å of Pd on 5000 Å of poly Si before and after annealing at 250 °C. After the heat treatment, the formation of an intermediate layer is revealed by the presence of the steps on the low-energy side of the Pd signal and the high-energy side of the Si signal. The amplitude ratio of these steps gives the atomic concentration ratio in this layer, which is found to be Pd:Si = 2.0:1.0. X-ray diffraction analysis establishes that the phase of this layer is Pd_2Si as is also found for the reaction of Pd on single-crystal Si at 250 °C.[3–6]

By measuring the width of the steps one can determine the thickness of the silicide layer.[7] Figure 5 shows the thickness of Pd_2Si as a function of time at four different temperatures. The abscissa is scaled in square root of time. Measured points are well fitted by straight lines through the origin. This shows that the rate-limiting process is the diffusion of the species through the silicide layer, as is the case for silicide formation on a single-crystal substrate.

Figure 6 shows the Arrhenius plot of the rate of Pd_2Si formation on the poly-Si substrate together with the result quoted by Bower *et al.*[4] for a single-crystal substrate. An activation energy of about 1.2 eV is obtained in the case of the poly-Si substrate. This value is 0.3 eV lower than the value obtained by Bower *et al.*, but is similar to the value of 1.27 eV reported by Hutchins and Shepalla.[5]

The poly-Si—Ni samples were annealed at temperatures between 225 and 325 °C and analyzed by backscattering. Figure 7 shows spectra of a sample with 5400 Å of Ni on 5000 Å of poly Si before and after annealing at

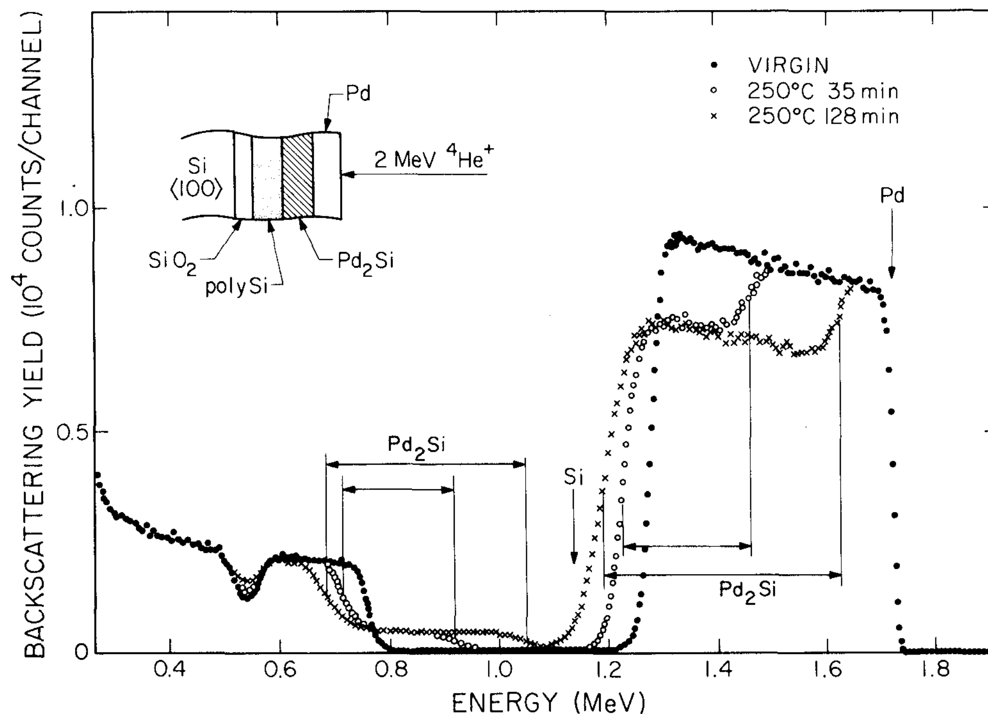

FIG. 4. Backscattering spectra of a 3700-Å film of Pd evaporated on 5000-Å poly Si before (●) and after annealing at 250 °C for 35 min (○) and 128 min (×). The arrows indicate the energy corresponding to scattering from atoms at the surface.

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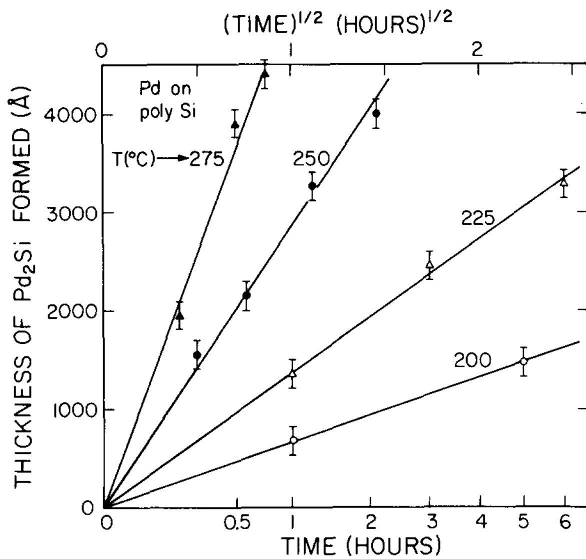

FIG. 5. Thickness of Pd_2Si formed in the reaction between Pd and poly Si as a function of time. The abscissa is scaled in square root of time.

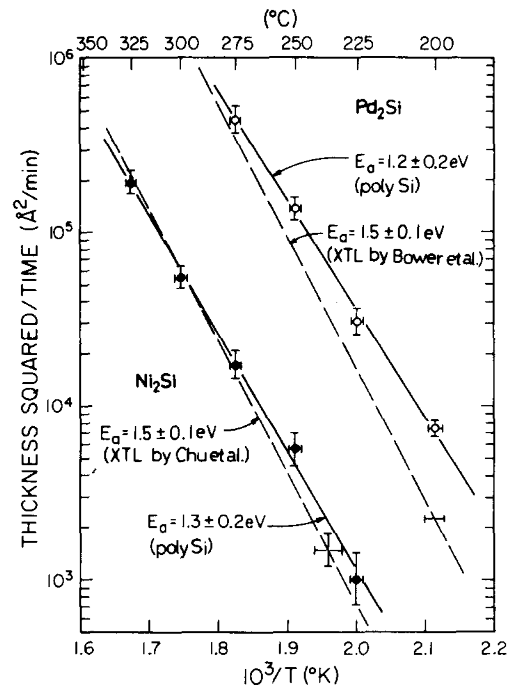

FIG. 6. Arrhenius plot for Pd_2Si and Ni_2Si formation in the reaction of poly Si with Pd and Ni. The formation rates for the case of a single-crystal substrate are also shown for reference purposes.

275 °C. As in the case of Pd, a silicide is formed. The amplitude ratio of the elements in the compound layer is found to be Ni : Si = 2.0 : 1.0. X-ray diffraction analysis identifies the phase as Ni_2Si as is found for the reaction of Ni on aingle-crystal Si in this temperature range. Growth curves are shown in Fig. 8.[8] The silicide, Ni_2Si, forms on the poly-Si substrate according to a parabolic time dependence, as is the case for a single-crystal substrate.[9] An Arrhenius plot of the formation rate of Ni_2Si is given in Fig. 6 and yields an activation energy of about 1.3 eV. This value is 0.2 eV lower than that found by Chu *et al.* for single-crystal substrate.[9]

Figure 9 shows the backscattering spectra of the sample with 1700 Å of Cr on 5000 Å of poly Si before and after annealing at 500 °C for 40 min. Analysis of this spectrum and x-ray diffraction measurements made on the sample after annealing indicate that $CrSi_2$ is formed, as in the case of the single-crystal substrate.[3] The growth kinetics of this system was not studied in

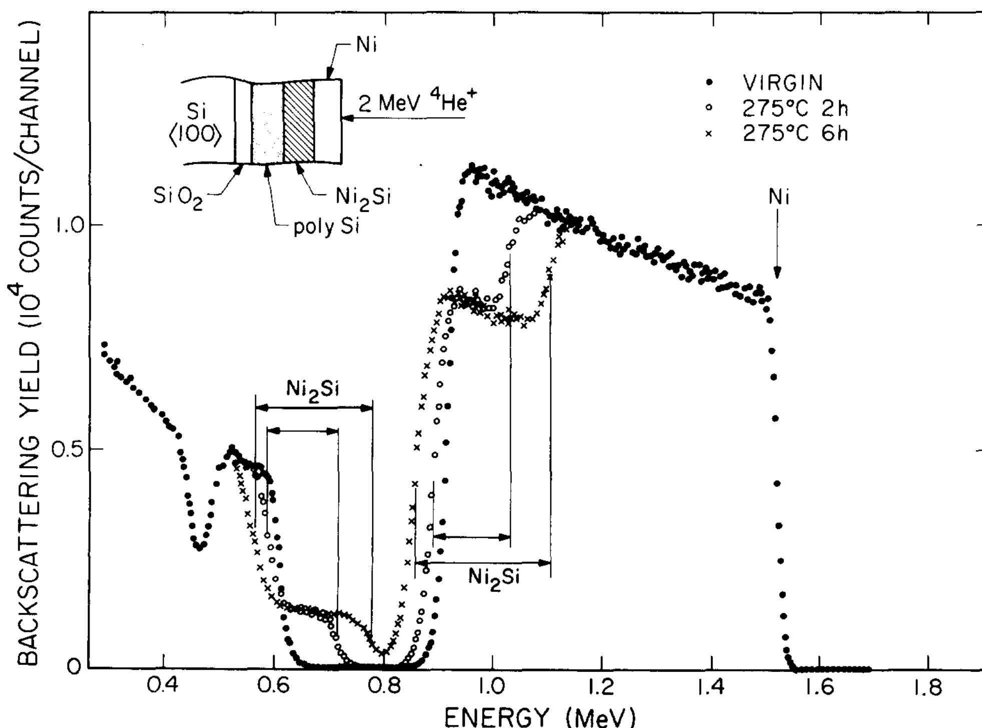

FIG. 7. Backscattering spectra of a 5400-Å film of Ni evaporated on 5000 Å of poly Si before (•) and after annealing at 275 °C for 2 h (○), and 6 h (×). The arrows indicate the energy corresponding to scattering from atoms at the surface.

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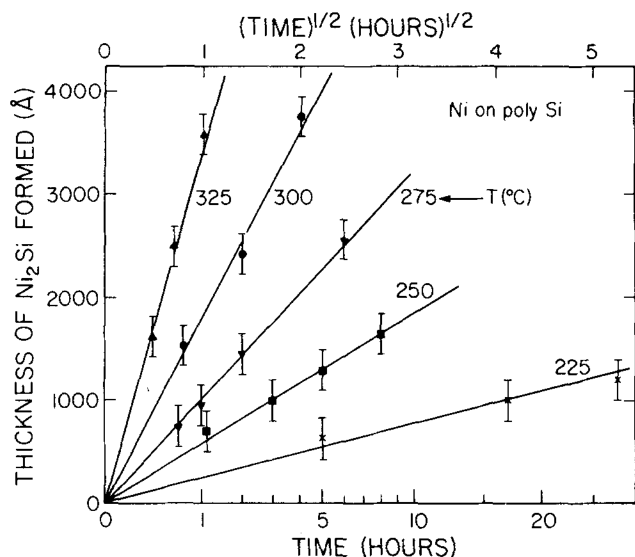

FIG. 8. Thickness of Ni_2Si formed in the reaction between Ni and poly Si as a function of time. The abscissa is scaled in square root of time.

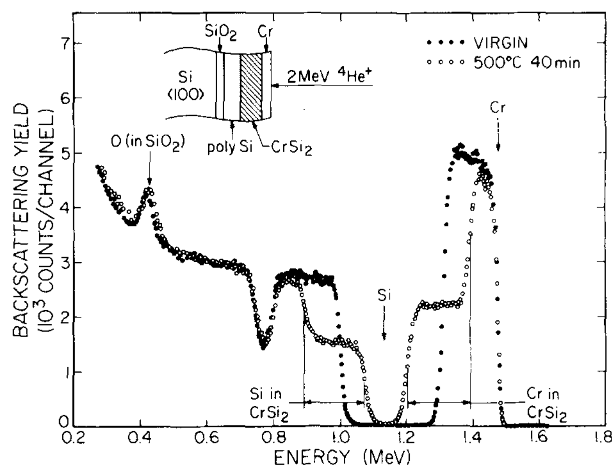

FIG. 9. Backscattering spectra of a 1700-Å film of Cr evaporated on 5000 Å of poly Si before (●) and after annealing at 500 °C for 40 min (○). The arrows indicate the energy corresponding to scattering from atoms at the surface.

detail, but silicide formation is observed in the same temperature range (450–500 °C) as that for single-crystal Si.[2,3]

In all three silicide forming systems there was no evidence of crystallite formation in the temperature range where growth of the silicide layers occurred. This is based on the absence of Debye-Scherrer rings corresponding to Si in the diffraction patterns and the presence of near-stoichiometric composition of metal to Si within the silicide layer.

IV. DISCUSSION AND CONCLUSION

For the case of Al, Ag, and Au, our results demonstrate that poly Si crystallizes below the eutectic temperature when in contact with films of these metals during annealing. The process thus seems to be a general one for metals forming a simple eutectic with Si.

This conclusion is plausible if one assumes that the force which drives this process originates from the growth of large-grain Si crystallites at the expense of the small-grained poly-Si material. That such a transformation actually occurs is clearly visible in Fig. 1. It is known, furthermore, from experiments by Hiraki *et al.* that Au films constitute an efficient transport medium for Si at temperatures as low as 100 °C.[10] Similar observations have been made on Ag films by Ottaviani *et al.*[11] It is worth noting also that the solubility of Si in Al is of the order of 1% at an anneal temperature of 500 °C,[12] while in Au it is less than 0.02% below the eutectic point.[13] The processes responsible for the crystallization are thus only weakly dependent on the solubility of Si in the metal. Transport along grain boundaries is a mechanism compatible with this fact, but our observations do not allow a conclusion regarding the micriscopic nature of the transport mechanisms involved.

In contrast to what is found for Al, Ag, and Au films, the crystallization of poly Si is not the dominant process for films of Pd, Ni, and Cr. Upon annealing, these metals form a silicide at the metal–poly-Si interface. There is no visible crystallization of the poly Si. The silicides formed are the same as those observed on single-crystal Si substrates. For the case of Pd and Ni, the growth kinetics also obeys the same time dependence ($\propto t^{1/2}$) found with single-crystal substrates, and the rate constants and the activation energies are quite similar (see Fig. 6). The kinetics of $CrSi_2$ formation has not been determined, but the temperature at which the compound begins to form on poly Si is close to that observed for single-crystal substrates also.

Once all the metal is consumed in the silicide, the structure is stable. No changes were observed after annealing for 20 h at the formation temperature. To see whether crystallization could be included at higher temperatures, a sample of about 4000 Å of poly Si covered with approximately 2000 Å of Pd_2Si formed at 270 °C was heated to 600 °C for 10 h. A comparison of the backscattering spectra taken before and after this second annealing revealed that some poly Si had moved to the surface. The result is reproducible. Generally, the changes seen in the spectra are consistent with an onset of poly-Si crystallization at the sample surface, but more detailed studies would be required to substantiate this conclusion.

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[1]K. Nakamura, M-A. Nicolet, J.W. Mayer, R.J. Blattner,

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and C.A. Evans, Jr., J. Appl. Phys. (to be published).

[2]J.W. Mayer and K.N. Tu, J. Vac. Sci. Technol. **11**, 86 (1974).

[3]R.W. Bower and J.W. Mayer, Appl. Phys. Lett. **20**, 359 (1972).

[4]R.W. Bower, D. Sigurd, and R.E. Scott, Solid-State Electron. **16**, 1461 (1973).

[5]G.A. Hutchins and A. Shepalla, Thin Solid Films **18**, 343 (1973).

[6]D.H. Lee, R.R. Hart, D.A. Kiewit, and O.J. Marsh, Phys. Status Solidi (a) **15**. 645 (1973)

[7]We have used $[S]_{Pd}^{Pd_2Si} = 109$ eV/Å to convert energy difference to thickness.

[8]We have used $[S]_{Ni}^{Ni_2Si} = 107$ eV/Å to convert energy difference to thickness.

[9]K.N. Tu, W.K. Chu, and J.W. Mayer, Thin Solid Films **25**, 403 (1975).

[10]A. Hiraki, E. Lugujjo, and J.W. Mayer, J. Appl. Phys. **43**, 3643 (1972).

[11]G. Ottaviani, D. Sigurd, V. Marrello, J.W. Mayer, and J.O. McCaldin, J. Appl. Phys. **45**, 1730 (1974).

[12]J.O. McCaldin and H. Sankur, Appl. Phys. Lett. **19**, 524 (1971).

[13]J.O. McCaldin, J. Vac. Sci. Technol. **11**, 990 (1974).

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