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INVESTIGATION OF SOLID-SOLID REACTIONS IN METAL FILMS ON SILICON

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Investigations were conducted on solid-solid reactions in gold films evaporated on silicon substrates at deposition temperatures below the eutectic point (370°C). Both air- and vacuum-annealed structures were studied using correlated data from transmission electron microscopy/diffraction (TEM/TED), Auger electron spectroscopy (AES) profiling, and forward current-voltage (I-V) measurements. Results of these experiments show that the grain size in Au films deposited (or annealed) at temperatures from 25°C to 200°C increases → over

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from 50Å (min) to a saturation size of approximately 1 μm at temperatures >150°C.

Significant intermixing of Au/Si occurs within the Au film and diffusion of Au into the Si substrate occurs at temperatures >100°C. Formation of silicides is initiated on the surface at grain boundary sites for temperatures >100°C. From AES and TED data, the composition of the silicide has been identified as δ-Au_3Si. For extended anneals at temperatures >330°C, additional silicides tentatively identified as the cubic alpha and gamma-phases have been detected. Correlated Schottky barrier-height measurements reflect the metallurgical changes occurring within mixing regions. Films deposited at temperatures >100°C show a significant reduction in oxide coverage for air-annealed samples and samples aged at room temperature. Vaccum-annealed samples (deposited at temperatures >100°C) show a reduction in subsequent intermixing, indicating the rate limiting effect of prior Au-Si mixing and silicide formation.

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INTRODUCTION

Metal-semiconductor contacts are usually formed by depositing a thin-metal film on the semiconductor substrate and then subjecting the structure to a heat treatment. Thin-metal films on single-crystal silicon have received the greatest attention because of the importance of these systems in silicon planar device technology where metal-silicon junctions are used to provide ohmic electrical contacts to device or to form Schottky barrier rectifying contacts.

The Au-Si system has been studied by a number of investigators.[1-5] It has been established that at temperatures > 150°C (below the eutectic temperature of 370°C), silicon migrates through Au thin-film layers and accumulates on the surface in the form of silicon dioxide. The oxide layer is nonuniform in thickness and its growth rate is influenced by both the oxidizing ambient and the crystallographic orientation of the silicon substrate. Recent results[5] obtained using Auger electron spectroscopy profiling on the Au-Si structure subjected to extended vacuum anneals have suggested that at temperatures >200°C, Au reacts with Si to form thin-layer (30Å) silicides at the surface. However, the composition of the silicides was only inferred from Auger spectral line splitting and amplitude ratio measurements. To date, no detailed studies have been undertaken of solid-solid reactions within the Au film or substrate mixing zone at temperatures significantly below the eutectic temperature. In this research program, we have attempted to provide a consistent investigation of Au-Si reactions using correlated data obtained from transmission electron microscopy/diffraction (TEM/TED), Auger electron spectroscopy (AES), and current-voltage (I-V) measurements.

This report contains results obtained during the first year's investigation. Data obtained in TEM/TED experiments and discussed in the six-month interim report are presented, accompanied by AES and I-V results from the second half of the program and an analysis of correlated data.

EXPERIMENTAL PROCEDURES

Polished, single-crystal Si wafers of (100) or (111) orientation obtained from Semi Metals Corporation were used for this study. The samples were n-type with resistivities ranging from 2.7 to 3.8 Ω-cm. The wafers were chemically cleaned and immersed in a dilute hydrofluoric acid solution to remove surface oxidation before depositing the Au thin films. Gold films ranging in thickness from 100 to 1000-Å were deposited on the silicon surfaces at a vacuum level of $\simeq 10^{-7}$ torr. Thickness of Au layers were measured by a quartz crystal monitor during deposition and subsequently checked with a multiple-beam interferometer after vacuum deposition.

Substrate temperatures were controlled by a sandwich-type heater and temperature monitor. The substrate heater consisted of a Mo filament placed between two quartz plates. During deposition, substrate temperatures were maintained in the range of 25° to 200°C. Postdeposition thermal anneals were done under vacuum or in air at temperatures up to 330°C for times varying from 5 min to 12 hr.

Annealed or "as-deposited" Au films were removed from the Si by dissolving the substrate in a solution of five parts HF and one part HNO_3. The film was removed from the solution with a 3-mm-diameter grid, and was subsequently rinsed and dried for TEM examination. In separate experiments, the Au film was stripped from the Si substrate using an aqua regia solution. The sample was then jet-thinned from the back

surface for TEM/TED analysis of Si-Au interfacial and mixing regions of the substrate. Annealed samples were prepared for TEM by first immersing the specimen in a dilute HF solution and then exposing it to ($KI + I_2$) and aqua regia solutions to remove SiO_2, Au + Si mixtures, and residual Au before jet thinning.

Since TED patterns from thin layers within interfacial or mixing zones are often obscure orill-defined, it was necessary to develop a technique for clearly and reproducibly imaging diffraction data. Using a radiotoning procedure, adapted from a technique described by Thackray et al.,[6,7] we intensified electron diffraction patterns recorded on Ilford plates and obtained autoradiographs on secondary plates to reconstruct the intensified diffraction data. This procedure has proven effective in these experiments and other studies of interfacial transitional zones of heterojunctions and will be discussed in detail in a separate paper to be published.

Samples used for electrical measurements were coated on the back surface with a 1000-Å-thick Au-Sb film and alloyed at 450°C for 30 min prior to deposition of Au films. Gold dots, 50-μm in diameter and 1000-Å thick, were vacuum-deposited on the front surface at substrate temperatures of 25°, 100°, and 160°C, respectively. After deposition, a number of samples were vacuum-annealed for 30 min at temperatures ranging from 150°C to 330°C. Air anneals were done in a tube furnace in the same temperature range.

Auger profiling of as-deposited and annealed structures was conducted in the vacuum chamber of an Auger spectroscopy unit obtained from Physical Electronics Inc. Single and dual Ar-ion sputtering guns were used to provide depth removal rates up to a maximum of 100 Å/min.

RESULTS

Transmission Electron Microscopy/Diffraction

Transmission electron micrographs were obtained on Au thin films evaporated on Si wafers at substrate temperatures ranging from 25° to 190°C. Representative bright-field electron micrographs are shown in Figures 1 and 2 for films evaporated at substrate temperatures of 100°C and 150°C, respectively. Average grain size measurements obtained from electron micrographs are summarized in Table 1.

Table 1

AVERAGE GRAIN SIZES IN Au FILMS EVAPORATED ON (100) Si WAFERS AS A FUNCTION OF Si SUBSTRATE DEPOSITION TEMPERATURE

Substrate Temperature (°C)	Grain Size (Å)
25	50 - 500
50	1000
100	2000 - 5000
150 - 160	<10,000
170 - 190	≥10,000

The data in Table 1 indicate that Au grain size increases rapidly as a function of increasing substrate temperatures from 25° to 160°C. At higher temperatures, the growth rate is substantially reduced, and apparent size saturation (≃1 μm) is obtained at temperatures below the Au-Si eutectic (370°C).

In a number of films deposited at substrate temperatures >100°C, we observed thin discontinuous overlaying deposits nucleated selectively at grain boundaries. Since these deposits are relatively thin compared

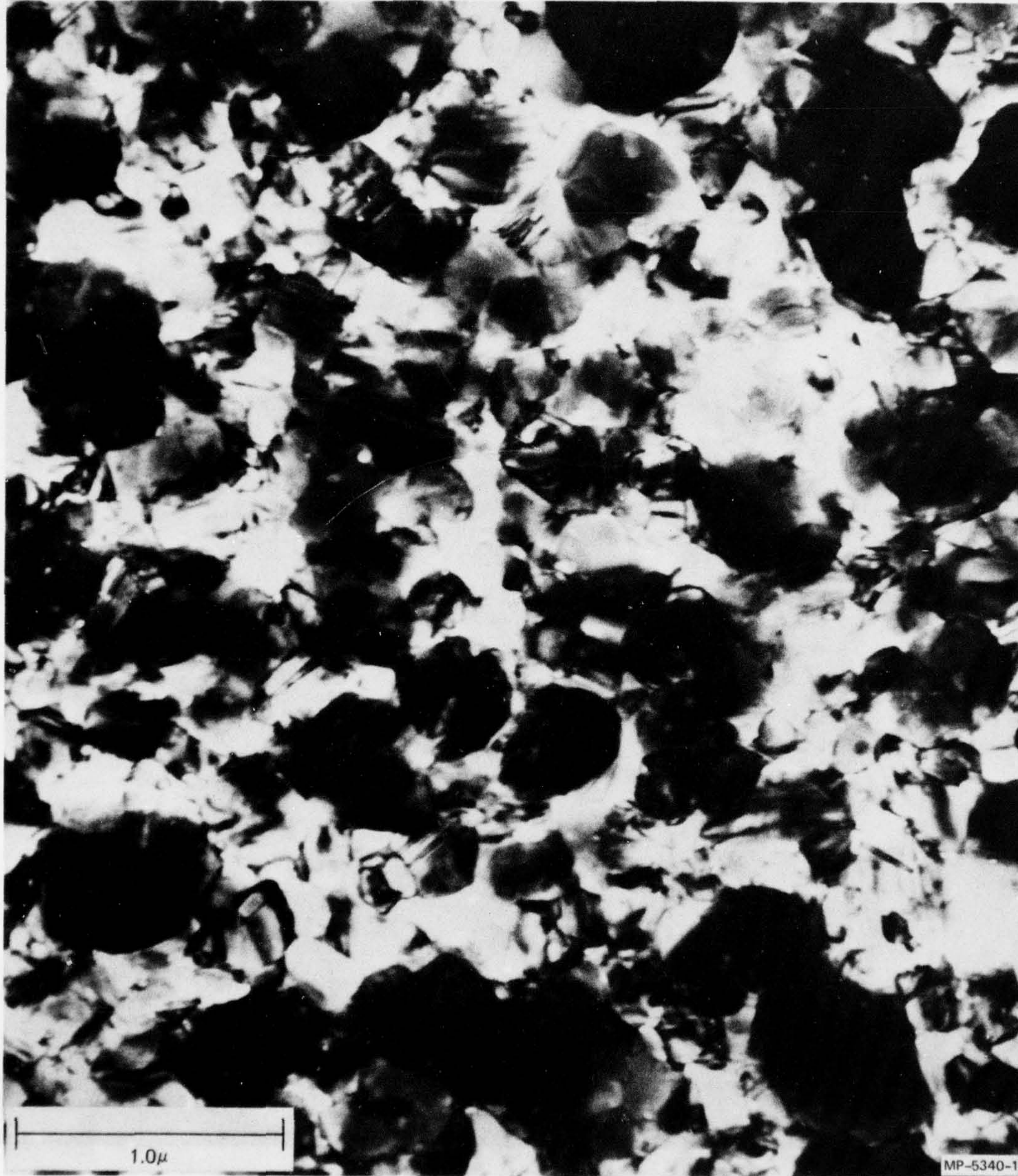

FIGURE 1 BRIGHT FIELD ELECTRON MICROGRAPH OF Au FILM EVAPORATED ON (100) SILICON AT SUBSTRATE DEPOSITION TEMPERATURE OF 100°C

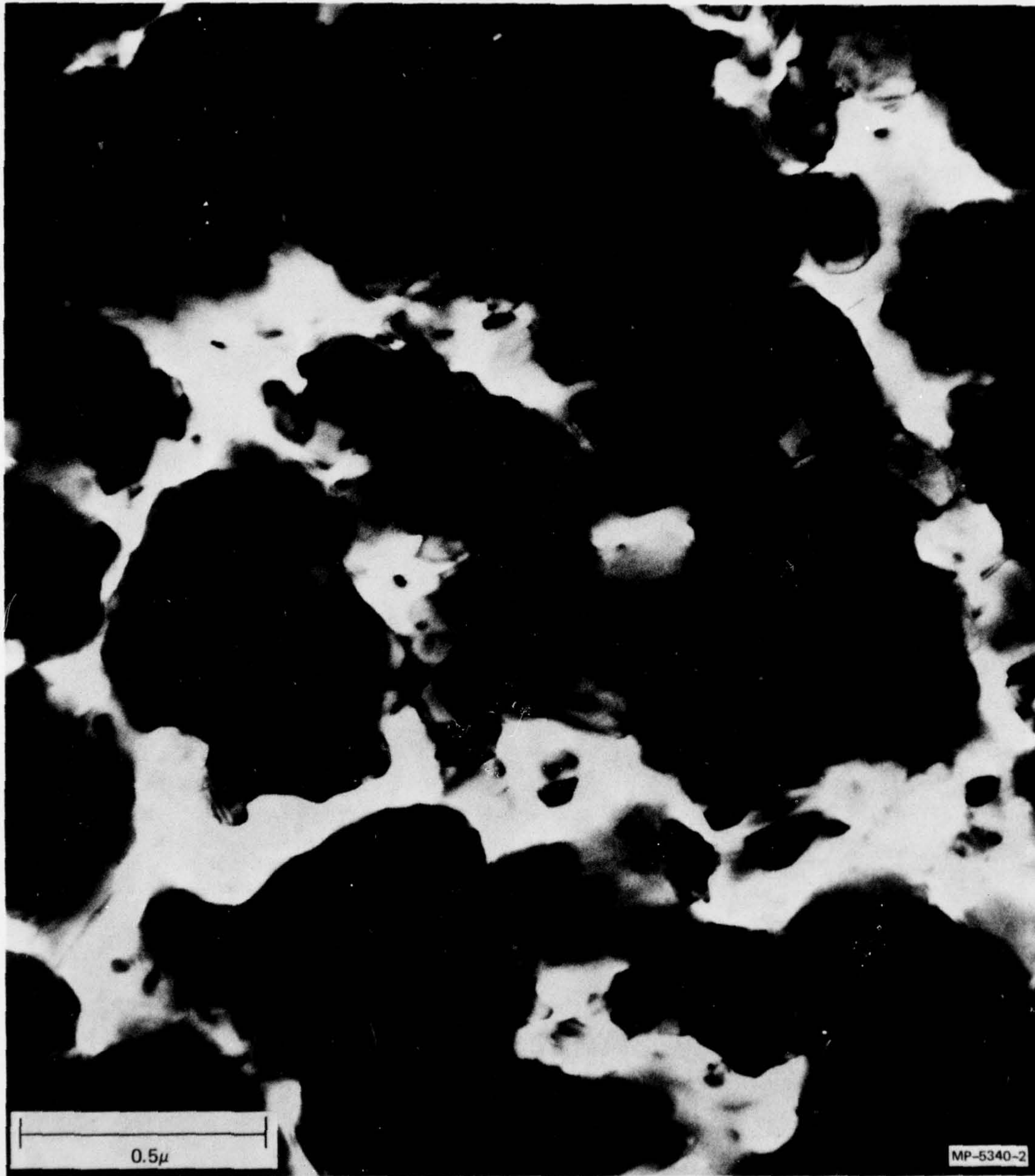

FIGURE 2 BRIGHT FIELD ELECTRON MICROGRAPH OF Au FILM EVAPORATED ON (100) SILICON AT SUBSTRATE DEPOSITION TEMPERATURE OF 150°C

with the thickness of the Au film, it has been extremely difficult to identify the exact composition of the overlayer by TED. It is possible that gold silicides are formed preferentially at the grain boundary regions. AES profiling data tend to support the existence of thin silicide layers at the surface, as will be discussed in the next section.

After the films were removed from the substrate with aqua regia, the as-prepared Si samples were thinned from the back surface for TEM analysis. Examination of interfacial and near-surface regions of the Si showed no detectable reactions or disordering of the lattice at substrate temperatures $<100^{o}C$. At temperatures $>100^{o}C$, diffraction patterns obtained from the mixing region exhibited a series of additional polycrystalline rings, as shown in Figure 3. Table 2 presents an analysis of data from this diffraction pattern and comparison with published data.[8] These data indicate that the second-phase crystallites are orthorhombic δ-gold silicide (Au_3Si) containing 17.9 atomic percent Si. Selected area electron diffraction patterns showed the presence of Au_3Si crystallites distributed throughout the Au-Si mixing region.

Au-Si structures prepared at variable substrate temperatures were annealed in a vacuum system at 10^{-7} torr to the eutectic point ($\approx 370^{o}C$) of the Au-Si system. TEM examination of the Au films revealed that grain growth occurs rapidly on structures annealed at temperatures $<200^{o}C$. Above anneal temperatures of $200^{o}C$, recordering is also observed at the top surface of the Au in the vicinity of grain boundaries. Mixing regions within the film and near-surface regions of the vacuum-annealed Au-Si structures were characterized by the presence of δ-phase gold silicide (Au_3Si) crystallites. The diffraction pattern and the analysis are shown in Figure 4 and Table 3, respectively. As the temperature and anneal time were increased, the number of crystallites and sharpness of diffraction rings also increased. In particular, the development of

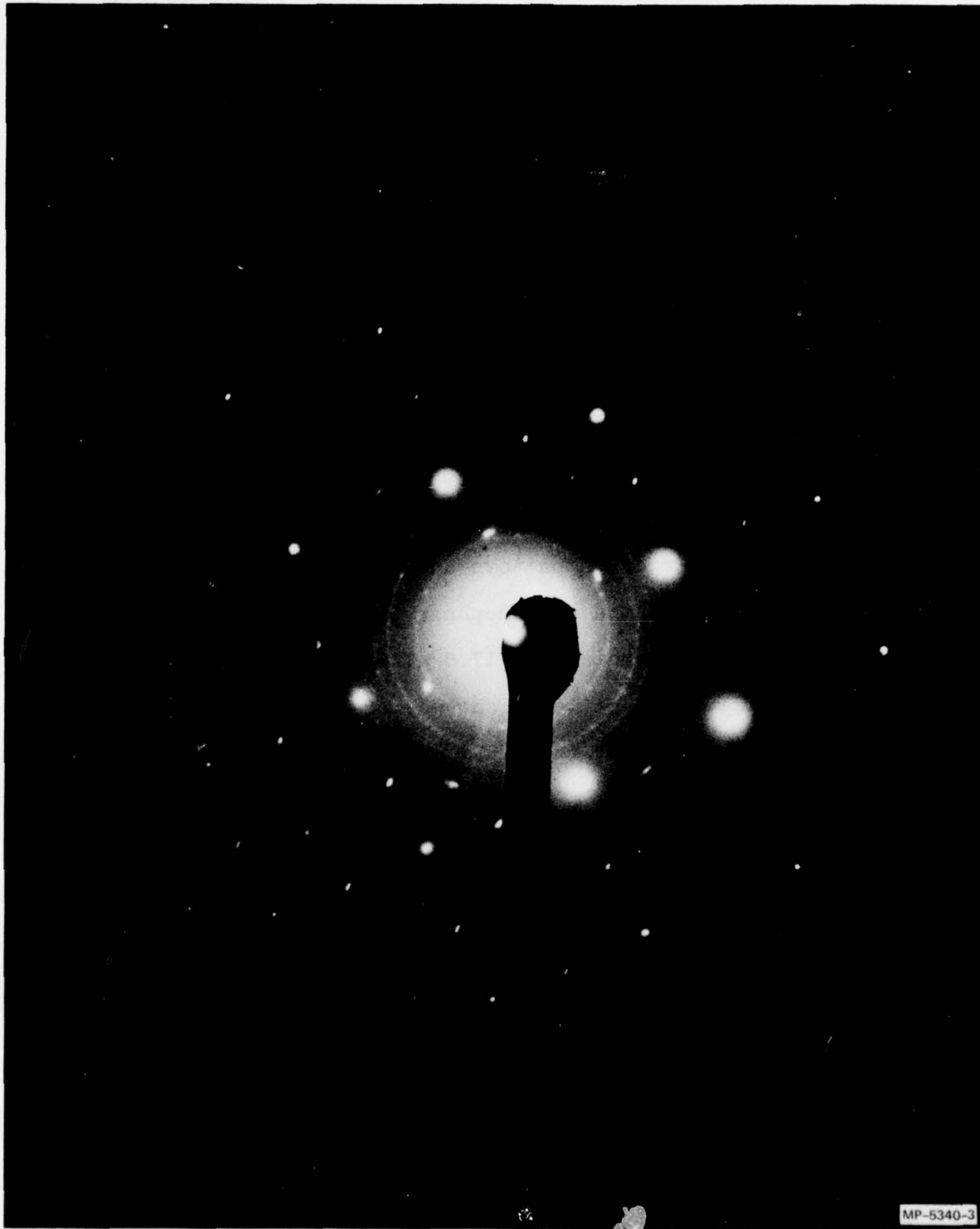

FIGURE 3 TRANSMISSION ELECTRON DIFFRACTION PATTERN OBTAINED FROM MIXING ZONE OF Au/Si STRUCTURE. SUBSTRATE DEPOSITION TEMPERATURE = 150°C; NO POST DEPOSITION ANNEAL. DIFFRACTION PATTERN ENHANCED USING RADIOISOTOPIC TONING TECHNIQUES

Table 2

ANALYSIS OF TRANSMISSION ELECTRON
DIFFRACTION PATTERN SHOWN IN FIGURE 3

Measured "d" Values	ASTM and Published "d" Values*	
	Si	δ Phase (Au_3Si)
3.195		3.195 (210)
3.116	3.116 (111)	
2.558		2.543 (301)
2.284		2.254 (220)
1.920	1.920 (220)	
1.637	1.638 (311)	
1.518		1.519 (126)
1.359	1.357 (400)	

*(hkl) values are given in parentheses.

Table 3

ANALYSIS OF TRANSMISSION ELECTRON
DIFFRACTION PATTERN SHOWN IN FIGURE 4

Measured "d" Values	ASTM and Published "d" Values*	
	Si	δ Phase (Au_3Si)
2.235		2.254 (220)
1.920	1.920 (220)	
1.368	1.359 (400)	
1.164		1.193 (228)
1.110		1.125 (440)
0.967	0.959 (440)	
0.888		0.874 (824)

*(hkl) values are given in parentheses.

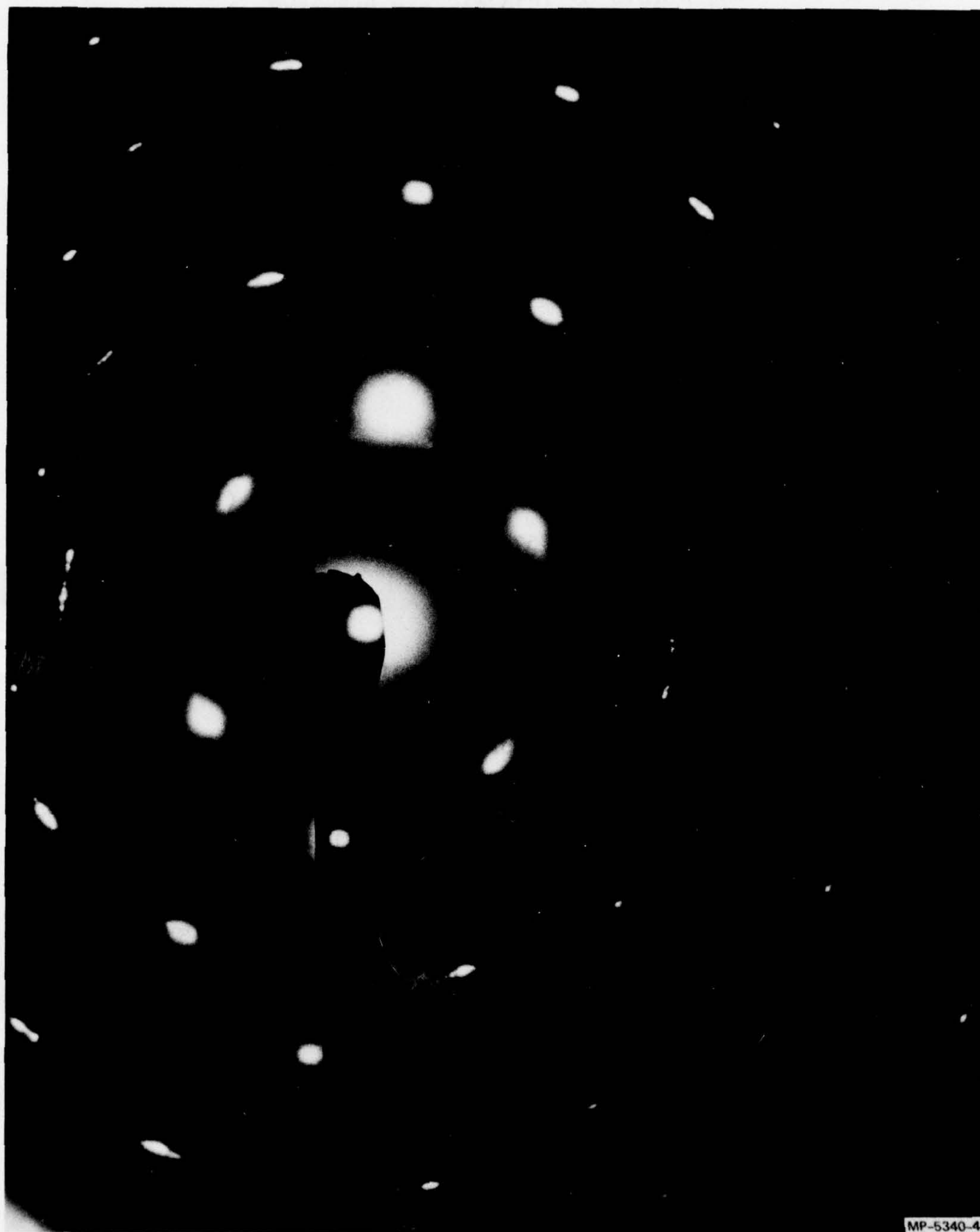

FIGURE 4 TRANSMISSION ELECTRON DIFFRACTION PATTERN OBTAINED FROM MIXING ZONE OF AN ANNEALED Au/Si STRUCTURE. SUBSTRATE DEPOSITION TEMPERATURE = 100°C; ANNEALED IN VACUUM FOR 30 MINUTES AT 330°C

Au_3Si crystallites was readily detected in samples annealed for long intervals slightly below the eutectic temperature.

In contrast to the results obtained for vacuum-annealed structures, a thick SiO_2 layer develops on the surface of gold films of Au-Si structures annealed in air. The thickness of this layer is proportional to the initial thickness of the Au thin film and the annealing time, in agreement with previous results.[4]

Within the mixing region reactions are often complex resulting in the possible formation of more than one phase of gold silicide. The δ-phase was identified, although a number of weak diffraction rings were observed that could not be correlated with either the δ-phase, Si, or Au. In an earlier paper, Anantharaman et al.[9] identified two face-centered cubic intermetallic phases of the Au-Si system, but unfortunately no detailed information was presented regarding indexing of the diffraction lines. We calculated "d" values of all possible reflections for the fcc lattice, using the published values for the lattice parameters of the α-phase ($a = 7.84$ Å) and the γ-phase ($a = 19.50$ Å). These data were then used to determine if measured "d" values obtained from diffraction patterns could be correlated with calculated values for the α-phases and γ-phases.

Figure 5 shows a representative diffraction pattern obtained within the mixing region of an Au-Si structure annealed in air at 400°C for 12 hr. Comparison of established and experimentally measured "d" values is shown in Table 4 and indicates good agreement for Si and δ-gold silicide lines. A number of additional lines can then be correlated with calculated d-values for the α- and γ-phases. However, the limited number of lines and the correlation with calculated rather than reported "d" values makes the identification of the α- and γ-phases very tentative. Since the appearance of more than one phase is noted within the mixing regions of all Au-Si structures annealed in air, we can assume formation

FIGURE 5 TRANSMISSION ELECTRON DIFFRACTION PATTERN OBTAINED FROM MIXING ZONE OF ANNEALED Au/Si STRUCTURE. SUBSTRATE DEPOSITION TEMPERATURE = 50°C; ANNEALED IN AIR FOR 12-HOURS AT 400°C

of the orthorhombic δ-phase and at least one or more additional intermetallic silicides, possibly similar to the α- and γ-phases.

Table 4

ANALYSIS OF TRANSMISSION ELECTRON DIFFRACTION PATTERN SHOWN IN FIGURE 5

	ASTM Published and Calculated "d" Values*			
Values (Å)	Si	α-Phase	γ-Phase	δ-Phase
5.540			5.629 (222)	
3.185	3.138 (111)			
3.049			3.083 (260)	
2.877		2.772 (021)		2.759 (020)
2.283		2.263 (222)		2.254 (220)
2.038			1.990 (844)	
1.915	1.920 (220)			
1.763		1.753 (420)		
1.636	1.638 (311)			
1.579				1.561 (107)
1.506				1.484 (430)
1.360	1.357 (400)			
1.289				1.272 (602)
1.234	1.246 (331)			
1.185				1.193 (228)

* (hkl) values are given in parentheses.

Auger Electron Spectroscopy

AES profiling analyses were obtained on "as-deposited" and vacuum- or air-annealed Au/Si samples as a function of temperature. Figures 6a to 6c show the results obtained on unannealed structures formed by vacuum deposition of Au at Si substrate temperatures of 25°C, 100°C, and 160°C, respectively. Figure 6a shows that room temperature deposition of the Au thin film produces no significant outdiffusion of Si into the Au layer. As the substrate temperature is increased (Figures 6b and 6c), Si diffuses rapidly into the Au film. At 100°C, Si has migrated to the surface of the Au and a mixed Au-Si film is formed. Similar experiments on structures annealed in vacuum at temperatures up to 330°C indicate that the amount of Si outdiffusion increases as the annealing temperature and annealing time increase. In all cases, there is a noticeable diffusion of Au into the Si substrate as a function of increasing substrate deposition and/or annealing temperature.

Figures 7a to 7c show AES profiles for Au films that have been deposited on Si at substrate temperatures of 25°C, 100°C, and 160°C, respectively, and annealed in air at 200°C. As the substrate deposition temperature is increased, significant intermixing of Si and Au occurs within the film and at the interface. The maximum near-surface concentration of oxygen is also present on films deposited at 20°C. At higher substrate deposition temperatures, the oxygen concentration is reduced, implying that the thickness of SiO_2 overlayers on Au/Si structures at moderate annealing temperatures is inversely proportional to the substrate temperature when the films were deposited.

We have also observed varying amounts of silicon and oxygen on the surfaces of films deposited at room temperature and allowed to age for several days in air. From AES profiles, the thicknesses of the oxide layers were determined to be ≃ 200 Å for samples deposited at room

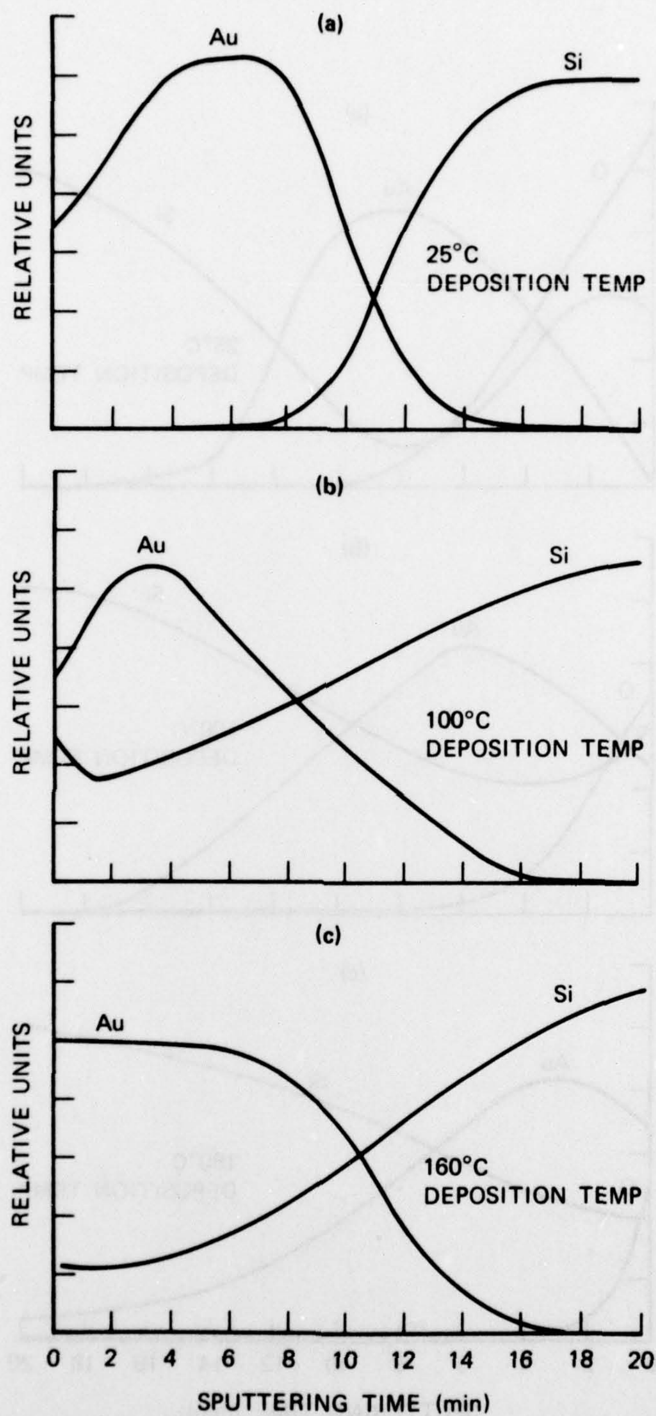

FIGURE 6 AES DEPTH PROFILES OF *Au/Si* STRUCTURES PREPARED AT VARIOUS SUBSTRATE DEPOSITION TEMPERATURES (NO ANNEAL)

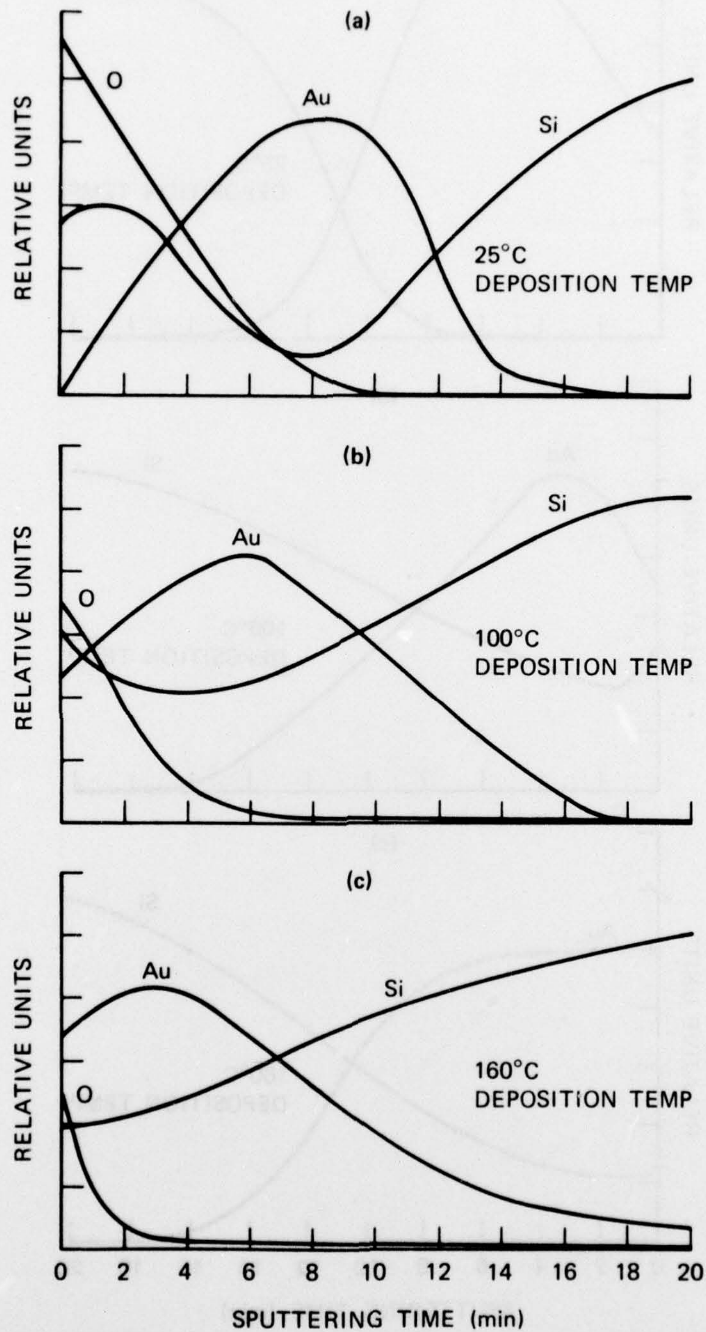

FIGURE 7 AES DEPTH PROFILES OF 200°C AIR ANNEALED (30 MINUTES) Au/Si STRUCTURES PREPARED AT VARIOUS SUBSTRATE DEPOSITION TEMPERATURES

temperature, $\simeq$ 50 Å for films deposited at 100°C, and $\leq$ 10 Å for layers deposited at 160°C.

For films deposited at room temperature, Si diffuses rapidly through the Au to accumulate at the surface. Annealing in air results in the formation of irregularly distributed oxides that reach a saturation thickness in proportion to the Au film thickness. Films deposited at substrate temperatures > 100°C exhibit a pronounced mixing phase and relatively inhibited growth of oxides at the surface. In addition, the mixed Au + Si phase within the film reduces room temperature thermal aging effects and the formation of oxides.

We observed two low energy Auger peaks that can be associated with the formation of silicides in as-deposited and vacuum-annealed (200°C, 30 min) films deposited at 25°C. These were positioned at 85 eV and 88.5 eV and are attributed to the splitting of the Si-LVV peak at 92 eV. In agreement with Green and Bauer,[5] we observed an apparent silicide thickness of $\simeq$ 35 Å at the surface of the film. However, our data indicate that the probable composition of the silicide in Au_3Si, as confirmed in direct identification from electron diffraction plates using radioisotopic image enhancement techniques.

Electrical Measurements

Schottky barrier measurements were used to investigate the behavior of Au films on Si substrates. Representative forward current-voltage (I-V) characteristics for samples prepared under various substrate deposition and annealing conditions are shown in Figures 8 to 10.

The thermionic emission theory for charge transport in Schottky barrier stuctures describes the barrier height, Φ_B, in the following equation[10]:

$$\Phi_B = \frac{kT}{q} \ln (A^{**}T^2/J_s) \quad (1)$$

where k is Boltzmann's constant; T is the absolute temperature; q is the electronic charge, A^{**} is, the effective Richardson constant; and J_s is the saturation current density.

Using Equation 1, the Schottky barrier heights were calculated from experimental data. In Figure 8, the barrier height for the Au film deposited at 25°C is 0.81 eV, in reasonable agreement with previously published results. At a deposition temperature of 100°C, Φ_B = 0.77 eV, and at 160°C, Φ_B = 0.64 eV. In all cases, J_s was observed to increase by several orders of magnitude as the deposition temperature increased from 25°C to 160°C.

The effect of 200°C vacuum annealing on charge transport properties of films deposited at variable substrate deposition temperatures is shown in Figure 9. As the substrate temperature is increased from 25°C to 160°C, the Schottky barrier height increases from 0.52 eV to 0.60 eV after annealing. The saturation current also exhibits a pronounced increase relative to unannealed samples deposited at temperatures < 160°C. The most pronounced variation, however, occurs for annealed samples deposited at 25°C. On these samples, the saturation current increases by approximately five orders of magnitude after annealing, corresponding to the development of a highly mixed region within the film and an apparent deep indiffusion of Au into the substrate. Correlated AES and TED data indicate that prominent mixing and silicide formation occur during deposition at substrate temperatures > 100°C. The I-V characteristics then suggest that the prior formation of Au-Si mixed phases during deposition will inhibit the outdiffusion of Si and subsequent motion of Au into the Si substrate during annealing. This conclusion is further supported by the similarity of I-V characteristics and saturation currents

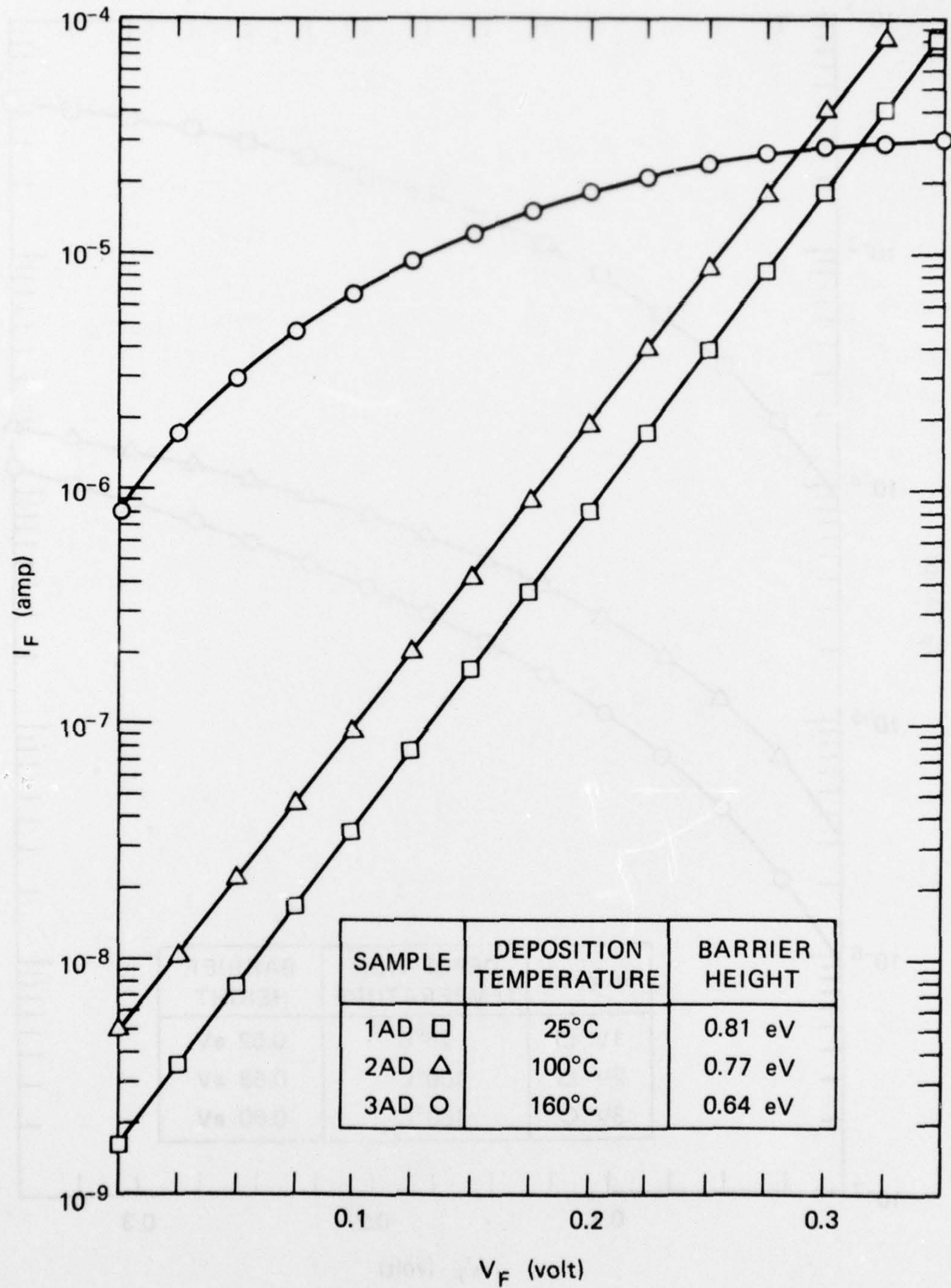

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FIGURE 8 FORWARD CURRENT-VOLTAGE CHARACTERISTICS OF Au FILMS DEPOSITED ON (100) Si AT VARIABLE SUBSTRATE TEMPERATURES (NO ANNEAL)

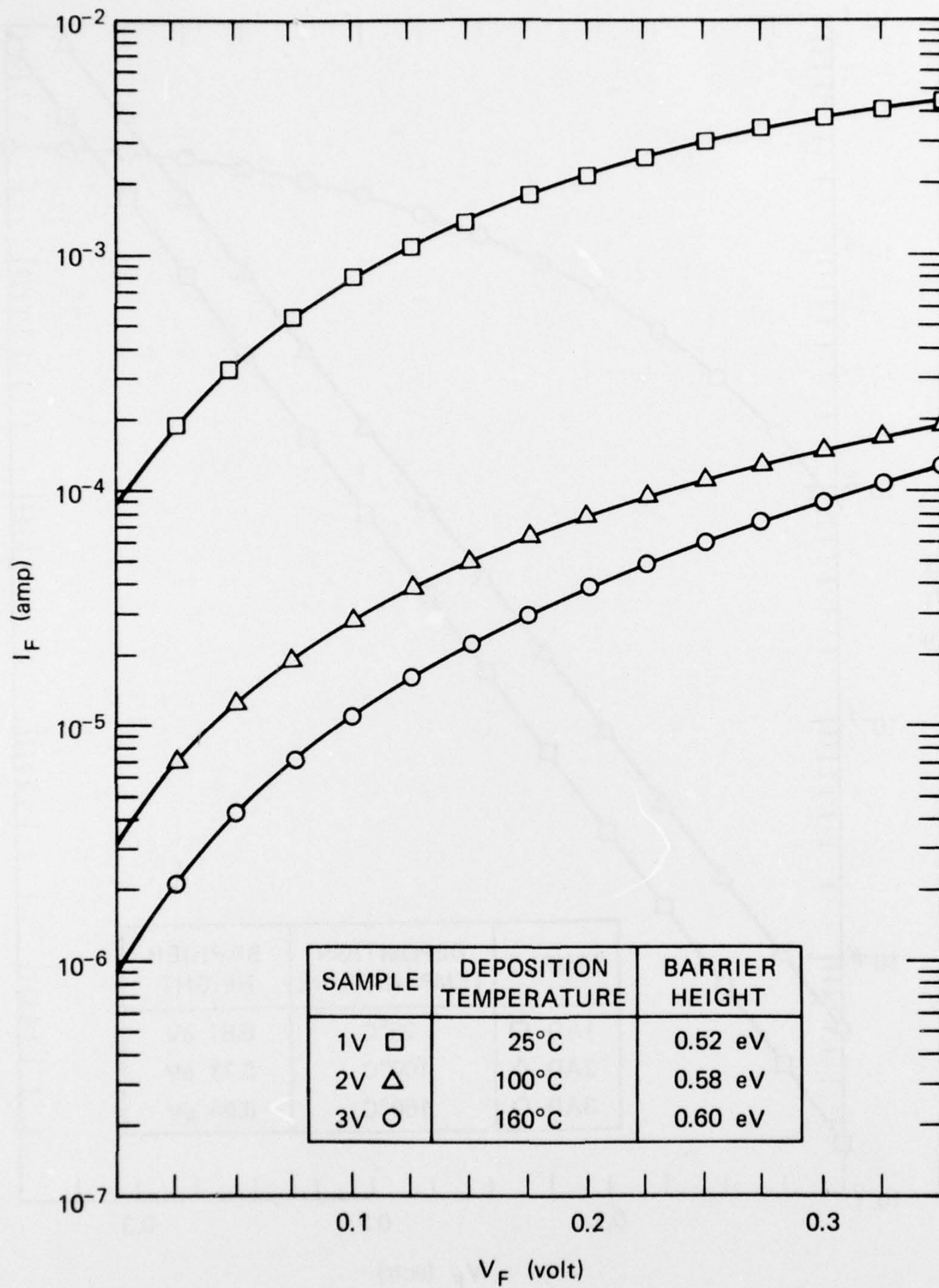

FIGURE 9 FORWARD CURRENT-VOLTAGE CHARACTERISTICS OF 200°C VACUUM ANNEALED (30 MINUTES) Au FILMS DEPOSITED ON (100) Si AT VARIABLE SUBSTRATE TEMPERATURES

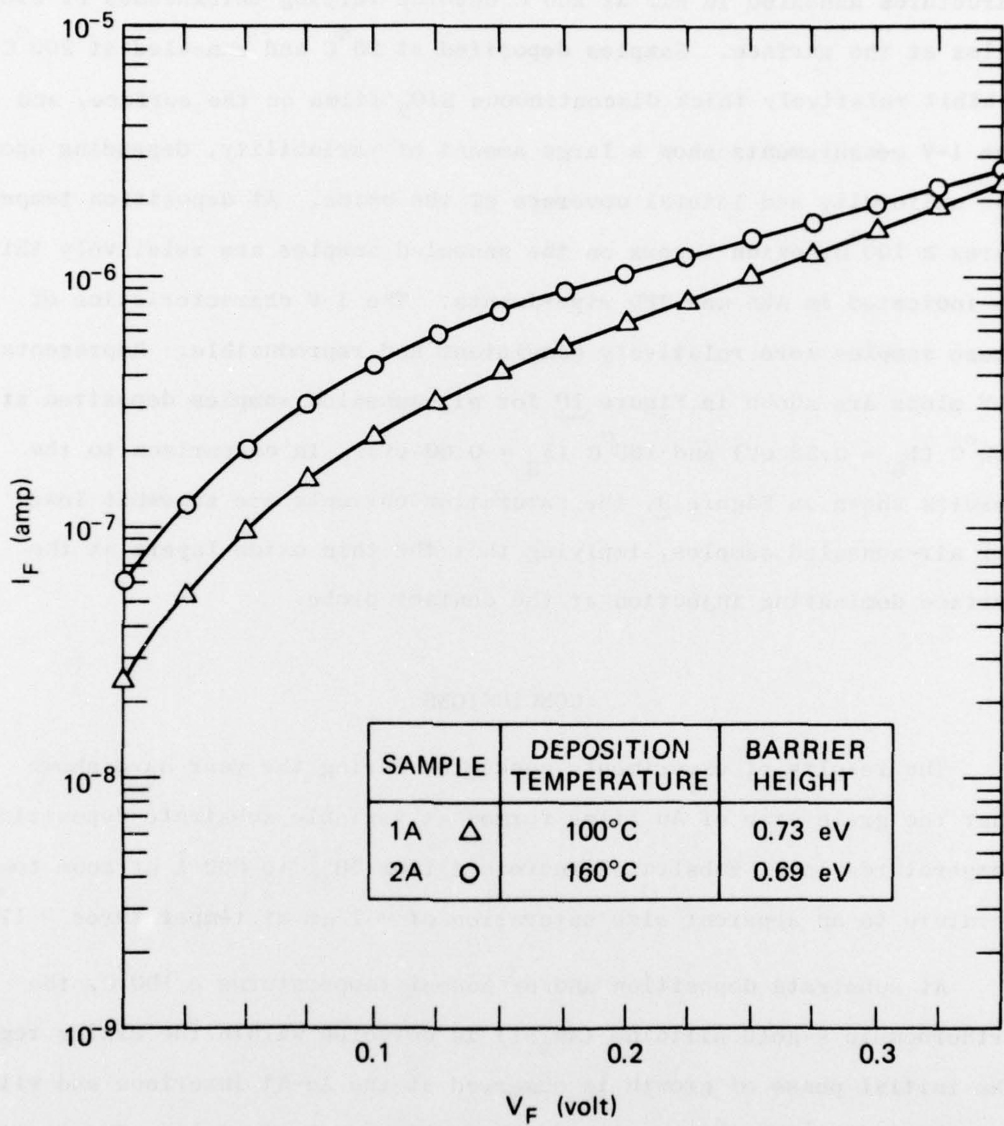

FIGURE 10 FORWARD CURRENT-VOLTAGE CHARACTERISTICS OF 200°C AIR ANNEALED (30 MINUTES) Au FILMS DEPOSITED ON (100) Si AT VARIABLE SUBSTRATE TEMPERATURES

for as-deposited and annealed samples deposited at 160°C.

In contrast to the results obtained for vacuum-annealed samples, structures annealed in air at 200°C develop varying thicknesses of SiO_2 films at the surface. Samples deposited at 25°C and annealed at 200°C exhibit relatively thick discontinuous SiO_2 films on the surface, and the I-V measurements show a large amount of variability, depending upon the uniformity and lateral coverage of the oxide. At deposition temperatures ≥ 100°C, oxide layers on the annealed samples are relatively thin, as indicated in AES and TED experiments. The I-V characteristics of these samples were relatively consistent and reproducible. Representative I-V plots are shown in Figure 10 for air-annealed samples deposited at 100°C (ϕ_B = 0.58 eV) and 160°C (ϕ_B = 0.60 eV). In comparison to the results shown in Figure 9, the saturation currents are somewhat lower for air-annealed samples, implying that the thin oxide layers at the surface dominating injection at the contact probe.

CONCLUSIONS

The results of experiments conducted during the year have shown that the grain size of Au films formed at variable substrate deposition temperatures on Si substrates increases from 50 Å to 500 Å at room temperature to an apparent size saturation of ≃ 1 μm at temperatures > 170°C.

At substrate deposition and/or anneal temperatures ≥ 100°C, the orthorhombic δ-gold silicide (Au_3Si) is detected within the mixing region. The initial phase of growth is observed at the Au-Si interface and within thin (≃ 35-Å thick) zones at the surface of the Au film. Correlated TEM and AES results suggest that the growth of the silicide as the surface of the film is initiated preferentially at grain boundary sites. At higher anneal temperatures (≥ 330°C), the appearance of the δ(Au_3Si) phase and at least one or more additional intermetallic silicides,

possibly similar to the α- and γ-silicide phases, is noted throughout the film.

At substrate deposition or vacuum anneal temperatures $> 100^{o}C$, Si outdiffuses readily into the Au film, producing a heavily mixed Au-Si region and Au indiffusion. Annealing in air produces similar Au-Si mixing zones and a discontinuous SiO_2 surface layer that increases in thickness as the Au film thickness increases. Growth of the oxide layer in annealed films deposited at substrate temperatures $\geq 100^{o}C$, however, is inhibited by the formation of mixing regions and silicides. In like manner, the development of oxide films during room temperature aging is more pronounced for films deposited at $25^{o}C$ and is negligible for films deposited at temperatures $> 100^{o}C$.

Correlated I-V measurements on samples deposited at variable substrate temperatures, and annealed in vacuum or air below the eutectic temperature, also reflect the metallurgical changes occurring within the Au film and at the Au-Si interface. At deposition (or vacuum anneal) temperatures $\geq 100^{o}C$, the development of prominent Au-Si mixing zones yields a reduction in Schottky barrier height and a marked increase in saturation current. Samples deposited at $25^{o}C$ and subsequently annealed in vacuum at $200^{o}C$ exhibit a larger increase in saturation current than those deposited at higher temperatures. The results indicate that the formation of silicides and intermixing regions during deposition will be rate-limiting for additional metallurgical changes during post-deposition annealing. In contrast, samples annealed in air will exhibit variable I-V characteristics relative to the vacuum-annealed samples, reflecting the varying thickness and discontinunity of SiO_2 layers at the surface of the air-annealed Au-films.

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