Thin Films and Solid-Phase Reactions

Traffic in a submicron world.

James W. Mayer, John M. Poate, King-Ning Tu

Thin films play a dominant role in modern technology. They appear as vital elements in integrated circuits as well as superconducting elements and solar energy conversion structures. Thin films are used both as active structures of precisely controlled thickness and area, and passive structures for connection to, or isolation from, the outside world.

In almost every application it is required that the thin film layers maintain structural integrity. However, it is generally observed that pronounced interdiffusion or phase formation can occur at remarkably low temperatures. Reaction temperatures as low as 23° to 200°C are found in some cases, while reactions in the range of 450° to 600°C are common. These reactions occur well below the melting point of any of the components or their eutectics in the thin film system and hence are called solid-phase reactions.

The impetus for much of the current work comes not only from technological imperatives but also from the accessibility of analytical techniques from such diverse fields as nuclear physics and surface science. These analytical techniques can provide composition profiles on a submicron scale, and have been used in the past 5 years for the study of solid-phase reactions in thin films. However, as early as 1935 Dumond and Youtz (*1*) pointed out the applicability of x-ray diffraction for studying low temperature, solid state diffusion in periodic thin film layers of Cu and Au. In their article they state, "it would seem likely that we have here an excellent way of studying intimately the diffusion of atoms in the solid state," and in a later work (*2*) they obtain the diffusion coefficients of Au through Cu at room temperature.

Similar techniques to these (*3*) and direct x-ray diffraction measurement of compound formation (*4*) or changes in optical reflectivity of evaporated films (*5*) have been pursued in the intervening years. However, here we will deal primarily with techniques that give us a direct measurement of reaction products in thin film systems.

As an example of a reaction which occurs at room temperature we show in Fig. 1 a picture of an Sn whisker that has grown spontaneously from an Sn layer deposited on a layer of Cu (*6*). Since the sample was deposited at room temperature and held at room temperature, there is no apparent force that would cause whisker growth. However, examination of the sample using some of the analytical techniques described below revealed that a Cu-Sn compound was formed at the interface between Cu and Sn at room temperature. The formation of the compound induced a compressive stress in the Sn layer—a stress that was relieved by the extrusion and growth of whiskers.

Crystal growth can be achieved in solid metal films at modest temperatures. The sketch and photograph in Fig. 2 show that Si can dissolve and form crystallites in an Au film (*7, 8*) at a temperature of 250°C. In the photograph in Fig. 2, the Au film has been etched away so that the Si crystallites are readily visible. Here the situation is analogous to growing crystals from a supersaturated liquid solution. The solid metal film acts as the solvent, and the fine-grained, polycrystallite Si layer as the source. The driving force is the reduction in surface energy which can be achieved by dissolving the small Si crystallites in the deposited layer and by forming large crystallites in the solid metal layer. This phenomenon has been extensively documented for amorphous semiconductor films in contact with metal layers (*9*).

The nucleation and growth of new phases in metal-semiconductor structures is so prevalent that they are used extensively in the formation of contact layers in Si devices (*10*). These silicide layers are formed at temperatures between 200° and 550°C. The problem that is usually faced is the prevention of further reactions with other metal films placed in contact with the silicide layers.

Comparison with Bulk Phenomena

In order to understand these solid-phase reactions in thin film structures, it is natural to attempt to relate them to phenomena in bulk samples. There is extensive experience accumulated on metallurgical reactions in large-scale, bulk samples. However, the very nature of the dimensions involved makes such comparisons difficult.

The usual measurements made on bulk samples characterize regions that are typically orders of magnitude larger than the submicron (100 to 1000 Å) thin film structures. Consequently, data on bulk samples are generally obtained at much higher temperatures or longer times than those characterizing reactions in thin films. Because of the relative scale one can reach equilibrium faster and at lower temperatures in thin film systems than in bulk samples.

There are several features that are unique to thin films that allow studies not readily achievable with bulk samples. Since distances are small, one can study not only reaction kinetics but also final states. In Au-Al thin films, for example, it is possible to monitor the growth and consumption of several distinct phases (Au-Al compounds) as the system approaches the final compound state (*11*). These reactions all occur at temperatures less than 200°C. Low temperature thin film reactions can also be applied (*12*) to determine the final state of a ternary system, especially when its phase diagram is not available. Next, since grain size in a thin film can be much smaller than that in bulk, grain boundary diffusion may dominate the kinetics in thin films. When grain size is about 100 Å in diameter, nearly 5 percent of the total atoms can be associated with grain boundaries (*13*). Since at low temperatures grain boundary diffusion is often more than two orders of magnitude faster than lattice diffusion, it is possible to determine the influence of grain boundaries on diffusion kinetics (*14*). In addition, thin films offer an opportunity to study interfaces. Such studies are often difficult to carry out in bulk systems where the interface can be buried deep within the sample. Conversely, in thin films the nature of the interface between two layers can completely dominate the behavior of the system. A thin (10 to 100 Å thick) oxide layer can often block phase formation at the normal reaction temperature (*15*).

Of course, these thin film systems introduce a whole set of problems that are often not encountered in bulk systems. We

---

Dr. Mayer is a professor of electrical engineering at the California Institute of Technology, Pasadena 91125. Dr. Poate is a staff member at Bell Laboratories, Murray Hill, New Jersey 07974. Dr. Tu is a staff member at IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.

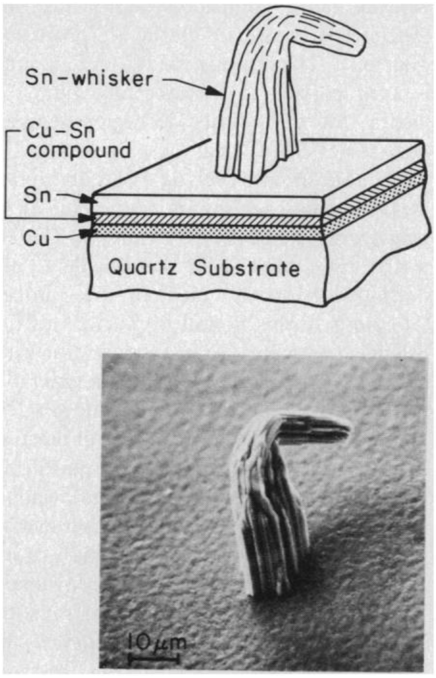


Fig. 1. The spontaneous growth of tin whiskers on the free surface of Sn in bimetallic Cu-Sn thin films stored at room temperature. The diameter of the whiskers is larger than the thicknesses of the Sn (2.5 μm) or Cu (0.6 μm) layers. [From Tu (*6*)]

have mentioned the key role of interface properties. In addition, because of the relatively small dimensions involved, oxygen or other impurities can diffuse into the structure and thus influence reaction rates (*16*).

In almost all studies of thin films, the structures are formed by vacuum deposition techniques. The films can be deposited on substrates by evaporation from filaments, by use of electron-gun evaporation techniques, or by sputter deposition. Unless stringent precautions are adopted, impurities can be incorporated within the structure during deposition. Also, the very fact of different thermal expansion coefficients between film and substrate can lead to high stress levels in the film. It has been shown that application of hydrostatic pressure to thin film structures can influence the reaction kinetics (*17*).

Characterization of Thin Films

From the considerations listed above, it is clear that it is necessary to characterize the properties of these thin film structures. It is also necessary to use techniques that have the requisite depth resolution, so that the kinetics of reactions occurring on a submicron scale can be measured with some precision. Therein lies the problem. The thickness range of 0.1 to 1 μm lies in a difficult region as far as conventional analytical methods are concerned. These thin film structures are too thin to apply conventional sectioning or x-ray analysis methods that have been used so successfully in metallurgical investigation of bulk samples. Conversely, the films are typically too thick to apply conventional transmission electron microscopy techniques.

Fortunately, over the past 5 years, analytical techniques have been developed which are capable of analyzing films in the thickness range of a few hundred angstroms (0.01 μm) to a few micrometers in thickness. Some of these techniques, such as backscattering spectrometry (*18*), have been known for over 20 years, but have only recently received serious attention as analytical tools. Other techniques, such as Auger electron spectroscopy, are primarily tools for surface analysis but have been adapted to depth profiling measurement by use of controlled layer removal (*19*).

The schematic diagram in Fig. 3 illustrates two general approaches to obtaining depth profiles. For the case in which nuclear techniques [backscattering (*20*), ion-induced x-rays (*21*), or nuclear reactions (*22*)] are employed (Fig. 3a), depth information is deduced from the energy loss of the energetic particles (usually protons or He ions) along their inward or outward tracks (or both). The depth resolution capability varies with the different techniques with about 0.02-μm depth resolution over depths of 0.5 μm for backscattering, and about 0.1 μm over 1-μm depths for ion-induced x-rays. The sensitivity to impurity concentration levels depends on the technique, with backscattering sensitive to high mass impurities and nuclear reactions sensitive to low mass impurities.

The other general approach to obtaining depth profiles is to use a surface analytical tool to determine the composition of the surface region and then to use a layer removal technique to expose underlying regions. Layer removal is generally accomplished by sputter etching, in which a beam of kiloelectron volt Ar or other gas ions is directed at the target to cause ejection of surface atoms (Fig. $3b_1$). Depth profiles are now routinely generated in commercially available instruments which use sputtering for layer removal and generally one of three surface analytical tools: Auger electron spectroscopy (AES) (*23*), secondary ion mass spectroscopy (SIMS) (*24*), or low energy backscattering techniques (Fig. $3b_2$) (*25*).

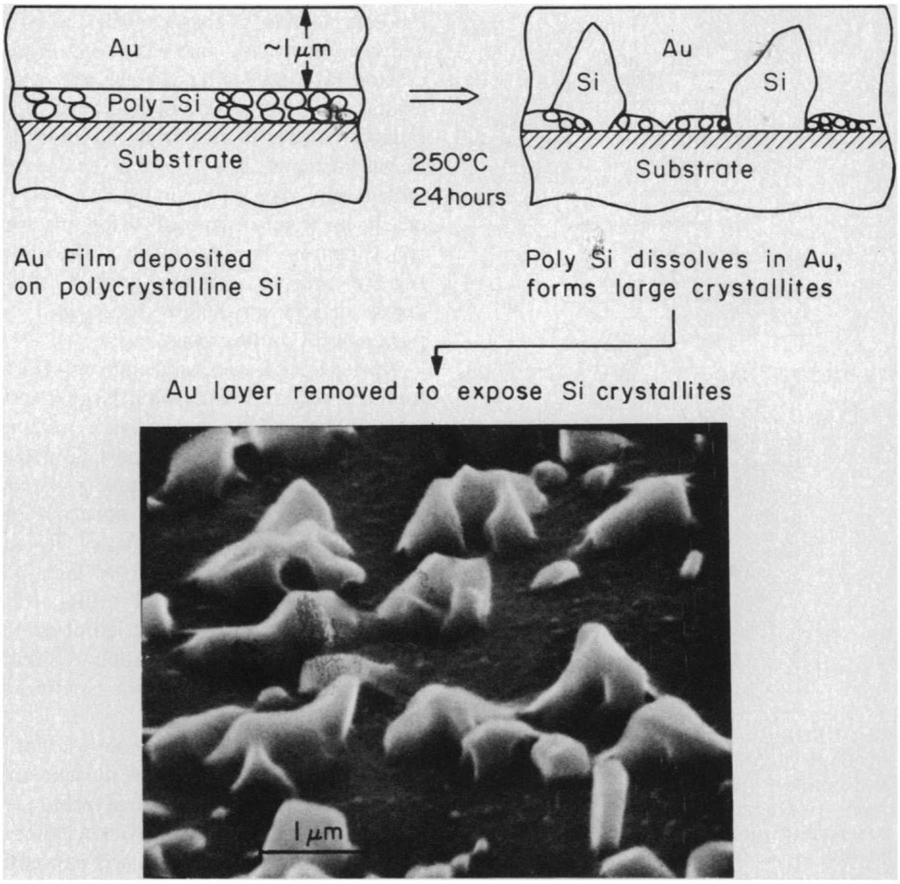


Fig. 2. Dissolution of a 0.3-μm-thick polycrystalline Si layer into a 1-μm-thick Au film and subsequent formation of large silicon crystallites. The scanning electron microscope view in the lower portion was obtained after the Au layer was removed. [From Nakamura and Lau (*8*)]

In order to compare the two analytical approaches we shall describe the data obtained from a silicide sample in which 2000 Å of Ni was deposited on an Si single crystal substrate and the composite structure annealed at 250°C for 24 hours (*26*). Figure 4 shows a backscattering spectrum for 2-Mev ^{4}He ions incident on the structure and Fig. 5 shows an Auger depth profile for which the primary electron beam (analysis beam) energy was 5 kev and the sputtering ion beam (layer removal beam) energy was 2 kev. In Fig. 4, the number of backscattered He particles incident on a particle detector is plotted versus the energy of the backscattered particles. The backscattering spectrum shows that the silicide layer (shaded portion) has not completely consumed all the Ni (unshaded portion). The energy width ΔE of the shaded portion of the spectrum gives the width ΔX of the silicide region [energy loss tables (*20, 27*) can be used to convert from ΔE in kiloelectron volts to thickness in atoms per square centimeter or in angstroms if a density is assumed]. The Ni to Si ratio of 2 : 1 in the silicide is determined from the ratio of the number of counts in the Ni and Si portions of the silicide spectrum using a straightforward correction for scattering cross section (*20*). In the Auger spectroscopy profile (Fig. 5) of the annealed sample, the outermost layer (from 0 to 6 minutes of sputtering time) is seen to be Ni and the composition ratio of the underlying silicide layer can be calculated from the Auger signals from pure Ni and Si surfaces. The conversion from sputtering time to thickness must be determined from similar samples of known thicknesses.

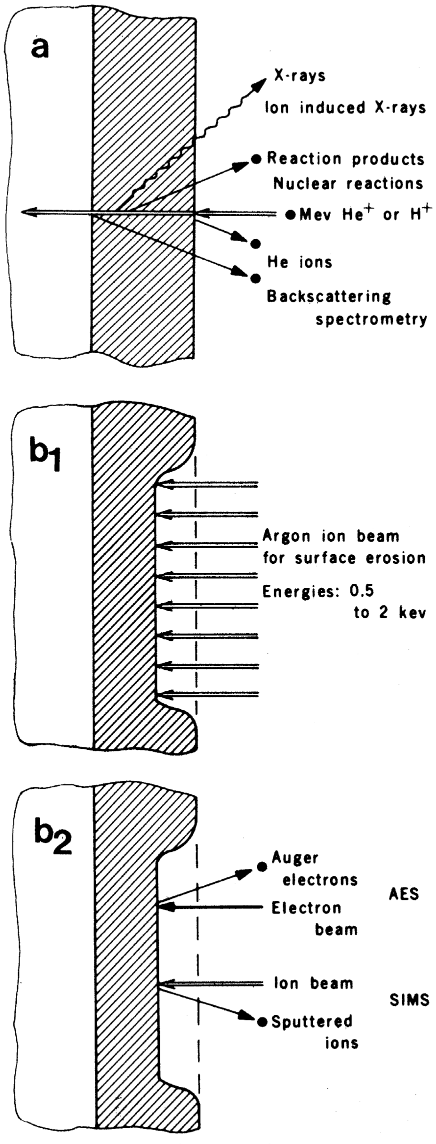


Fig. 3. Schematic diagram of two approaches to obtain depth profiles in thin film structures. (a) With nuclear techniques, the thickness of the layers is determined from the energy loss of energetic particles. (b_1 and b_2) A two-step process in which controlled thicknesses of the layer are eroded away by sputtering with Ar ion beams (b_1) and then the composition of the surface layer is analyzed by surface-sensitive techniques (b_2).

On a more general basis, we can compare nuclear techniques which rely on energy loss of the probing energetic ions for depth information, and surface analysis techniques that rely on sputtering rates for depth profiles. Sputtering techniques require calibration to establish the erosion rate. Preferential sputtering effects in alloys or compounds can lead to changes in the composition of the near surface layer which is analyzed, and variations in the erosion rates across the surface of a polycrystalline region result in significant degradation of depth resolution. In addition, the surface analysis techniques require calibration by use of standard samples of nearly identical composition for absolute concentration measurements. However, relative measurements can be made of the depth variation of the host atoms and impurities on a routine basis.

Nuclear techniques, while more straightforward, require a somewhat large investment in equipment, typically, a million-electron-volt accelerator, a particle detection system, and a data processing system. All of these are common in most nuclear laboratories. Nuclear techniques do not require sample erosion, and by their nature provide absolute measurements of the target composition as a function of depth. Data acquisition is faster, about 15 minutes per sample, than with sputtering methods.

Recent investigations have shown that it is advantageous to use both nuclear and surface plus stripping analytical techniques (*28*). Nuclear techniques provide a calibration of the sample thickness and composition, while surface analytical techniques give relative concentrations and impurity distributions. However, even on an individual basis, both methods have been used with great success in investigations of thin film reactions.

These two microanalytical methods give composition and impurity depth profiles within thin film structures. However, we also need information on phase identification, crystal structure, and stress. For this purpose it has been possible to adapt conventional x-ray techniques by using glancing incidence as shown in Fig. 6. By using this approach we effectively increase the film thickness by an order of magnitude, as compared to the conventional normal incidence. Two systems, the Seemann-Bohlin diffractometer (*29*) and the Read camera (*30*), have been developed on this principle and are capable of identifying compound phases of thickness between 100 and 300 Å. The diffraction peaks shown in the lower portion of Fig. 6 were obtained with a Seemann-Bohlin system and can be identified with Ni and Ni_2Si reflections (*26*). Figure 7 shows the diffraction pattern obtained from a 2000-Å superconducting Nb_3Ge film on a sapphire substrate with a Read camera (*31*). The rings can be identified with reflection from the A15 structure of Nb_3Ge (in polycrystalline form) and the spots from the single crystal sapphire substrate. It is now well established that it is advantageous to use both depth profiling and x-ray diffraction techniques to characterize deposited and reacted thin film structures (*32, 33*).

Of course, we do not neglect the more conventional tools such as scanning electron microscopy or the electron microprobe. These are routinely used to determine lateral variations in the sample structure. Then, too, with specially prepared samples, transmission electron microscopy gives insight into crystal and defect structures, and may prove to be extremely useful in examination of interface regions.

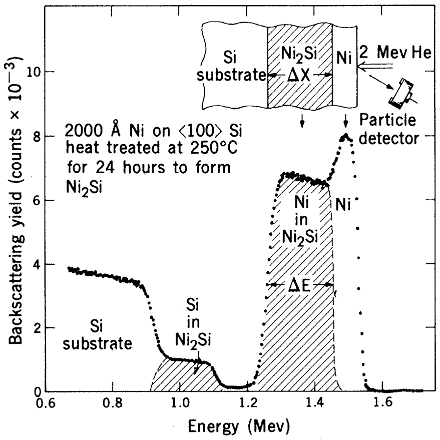
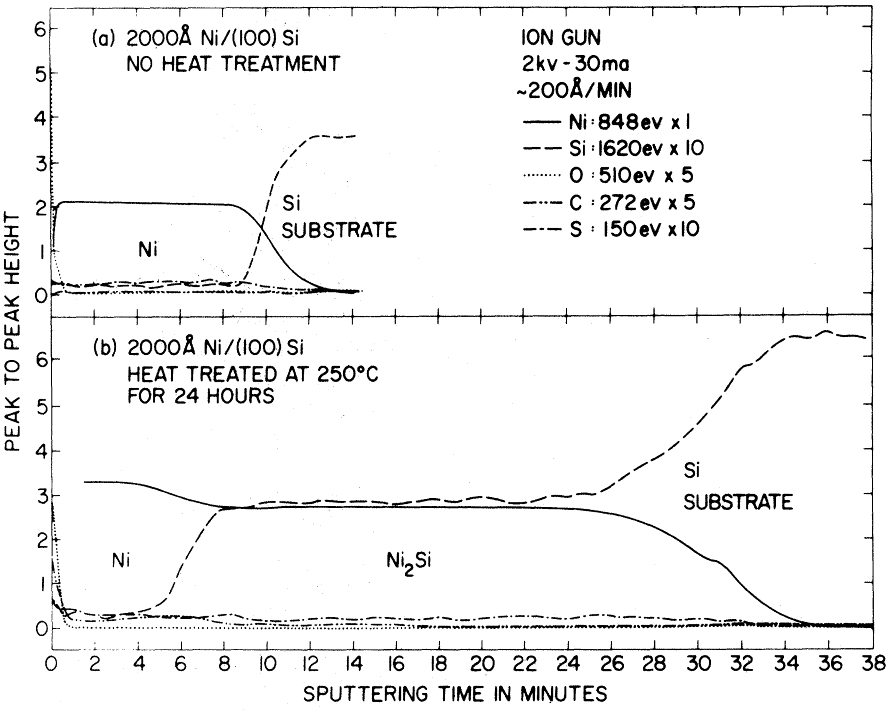


Fig. 4. Backscattering spectrum for 2-Mev He ions incident on a sample containing a layer of Ni_2Si (shaded region) formed by depositing Ni on a Si substrate and then heat treating at 250°C. [From Tu *et al.* (*26*)]

Fig. 5. Auger depth profile of the heat-treated sample analyzed by backscattering spectrometry in Fig. 4. Layer removal was made by sputtering with 2-kev Ar ions and surface analysis by Auger electron spectroscopy. (a) Shows analysis of the sample as deposited and (b) analysis of the same sample after heat treatment. [From Tu *et al.*; courtesy of *Thin Solid Films* (*26*)]



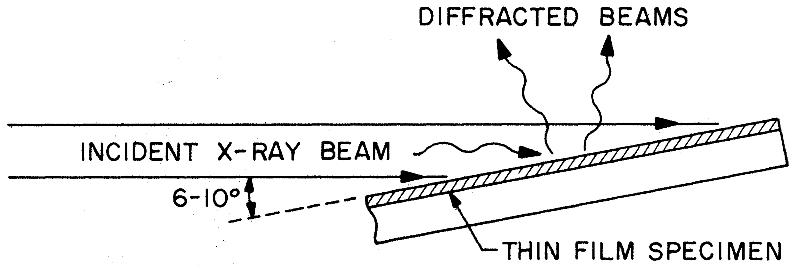
However, it is basically the development of the three tools—nuclear techniques, surface analysis plus layer stripping, and glancing angle x-ray diffraction—that has caused the surge of studies in thin film reaction studies.

An example of the application of these techniques is the analysis of deposited superconducting films and correlation of their superconducting and structural properties. The discovery that Nb_3Ge film can have a superconducting transition temperature (T_c) $\sim 22°$ to 23°K has given some impetus to the area. It is conventionally assumed that A15 thin films demonstrate high T_c's when they are close to the A_3B stoichiometry. However, x-ray diffraction (shown in Fig. 7) and backscattering investigations of a wide variety of sputter deposited Nb-Ge films show that, although the films appear to be predominantly a single phase, composition can deviate significantly from the stoichiometric Nb_3Ge value and yet they still possess high T_c's (*31*). It is hoped that studies such as these can lead to a better understanding of high T_c thin films.

Solid-Phase Reactions

Silicides. One of our first observations of thin film reactions is that well-defined, laterally uniform layers can be formed in many systems where phase formation occurs. The laterally uniform nature of silicide formation, for example, is shown in photographs (Fig. 8) of samples cleaved at low temperatures to avoid smearing the interface. The upper view of the deposited structure shows a layer of amorphous Si on a 2000-Å-thick Pd layer deposited on <100> oriented single crystal Si. After reaction at 280°C, the compound Pd_2Si is formed. Considering the polycrystalline nature of the silicide films, it is quite remarkable that uniform layers grow.

Silicides are important as contact layers in microelectronic integrated circuit technology, and consequently there have been many studies of metal film–Si systems (*33*). The initial work focused on growth kinetics and activation energy. One of the surprising features, in view of the high covalent bonding energy of Si atoms, was that solid-phase reactions could occur at



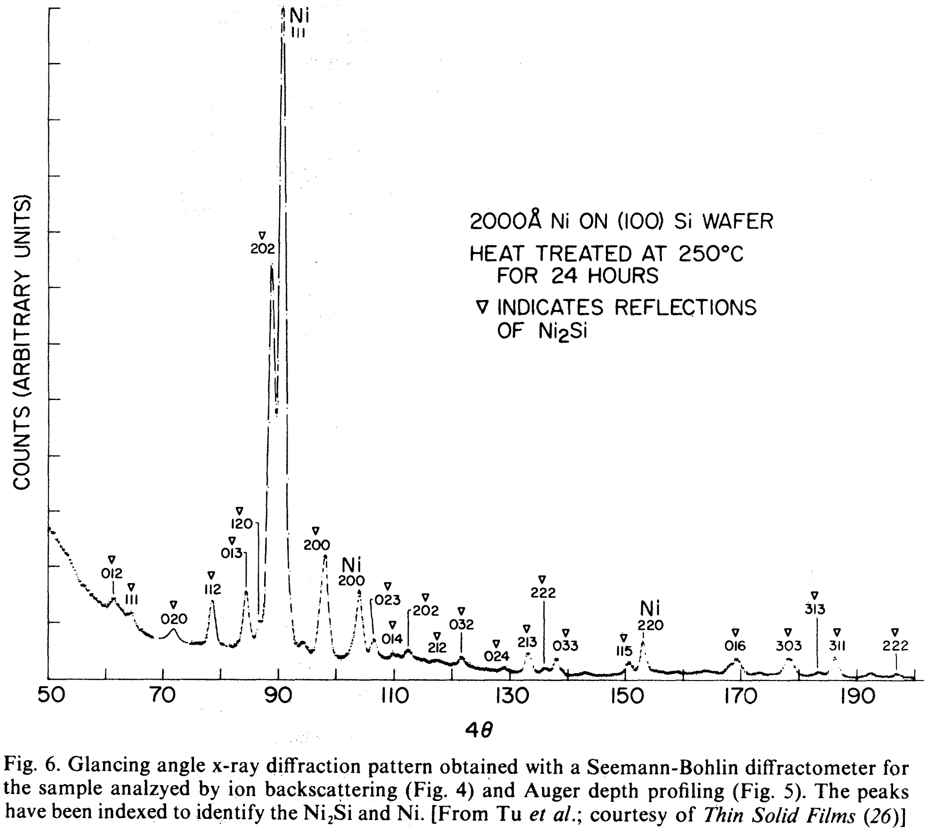


Fig. 6. Glancing angle x-ray diffraction pattern obtained with a Seemann-Bohlin diffractometer for the sample analzyed by ion backscattering (Fig. 4) and Auger depth profiling (Fig. 5). The peaks have been indexed to identify the Ni_2Si and Ni. [From Tu *et al.*; courtesy of *Thin Solid Films* (*26*)]

relatively low temperatures. For example, Ni, Pd, and Pt silicides form at 200°C, while the melting point of Si is about 1400°C (and even the melting point of these silicides is well above 700°C). This low formation temperature has led one of us to propose (*34*) that the noble and near-noble metal atoms can be incorporated on interstitial sites in the Si lattice to sufficiently high concentrations that the Si bonds at the interface change from covalent to those resembling metallic bonds. Since an interstitial increases the number of nearest neighbors of its host atoms, an Si atom at the interface with a high concentration of interstitials will have more than four nearest neighbors and will be bonded by unsaturated rather than saturated covalent bonds. The unsaturated covalent bonds are similar to metallic bonds and can be broken with a much higher frequency at low temperature than saturated covalent bonds.

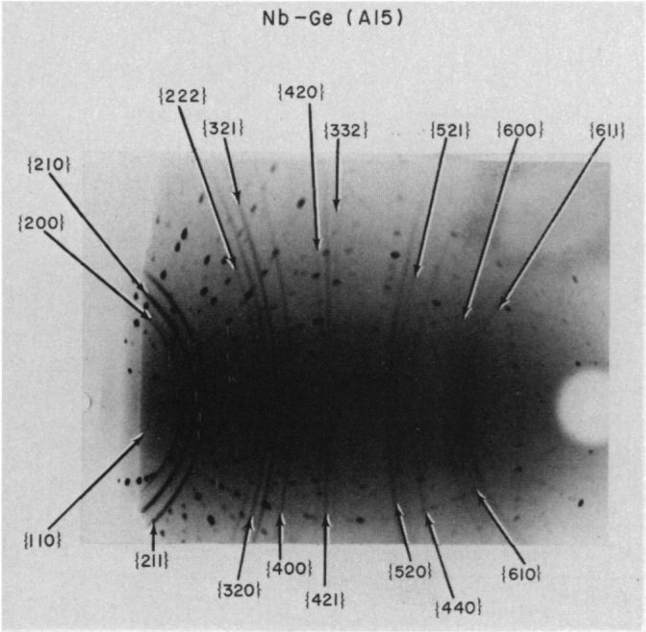
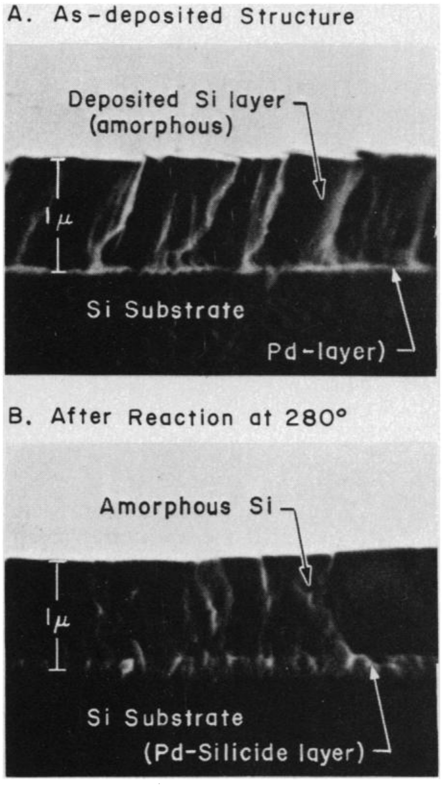


Fig. 7. Glancing angle x-ray diffraction pattern obtained with a Read camera for a 2000-Å-thick film of Nb$_3$Ge deposited on a sapphire substrate. The rings have been indexed to identify the polycrystalline Nb$_3$Ge and the spots are from the single crystal sapphire substrate. [From Testardi *et al.* (*31*)]



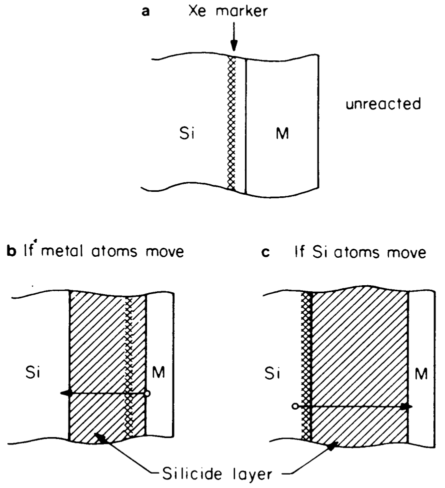


Fig. 8 (left). Scanning electron microscopy photographs of an edge view of a cleaved sample of 1 μm of Si deposited on 0.02 μm of Pd on a Si substrate. (A) Shows the As-deposited sample and (B) shows the sample after heat treatment at 280°C to form the phase Pd$_2$Si. Fig. 9 (right). Concept of using implanted rare gas ions as Kirkendall markers to identify the diffusing species in formation of silicide layers. (a) Metal film M evaporated onto a silicon substrate implanted with a Xe marker; (b) if Si atoms are the moving species the Xe marker will appear near the silicide-silicon interface; (c) if metal atoms are the moving species during compound formation, the Xe marker will shift toward the surface. The displacement of the markers can be measured by backscattering spectrometry. [From Chu *et al.*; courtesy of *Appl. Phys. Lett.* (*36*)]

In studies of diffusion and compound formation in bulk samples, diffusion markers have played a key role. Radiotracer techniques were developed for studies of host and impurity diffusion in crystals. Kirkendall markers (*35*), usually fine Mo or W wires placed at the interface between two metals, are used to determine which of the two metals diffuses through the compound during phase formation.

For thin film systems, it is also necessary to find diffusion markers. Embedded thin wires are not the answer because the wire diameter would have to be of the order of 100 Å if we are to study phase formation in 1000-Å-thick films. However, it is possible to implant Xe atoms into the structures and to monitor the displacement of the Xe during compound formation (*36*). The concept of the use of markers is shown in Fig. 9. By determining whether the Xe is displaced toward or away from the sample surface, we can find whether Si or the metal atoms diffuse across the compound during reaction. In many instances of silicide formation, Si is the diffusing species, but in others, particularly the phases which form at lower temperatures, the metal atoms move. For example, Ni-Si forms at 200°C by diffusion of Ni atoms, while Ti-Si forms at 600°C by diffusion of Si atoms across the compound (*36*).

We find that kinetics are the major consideration in the initial stages of silicide formation. Although many phases are given in the equilibrium phase diagram, usually only one phase nucleates and grows (*33*). In the later stages (at higher heat-treatment temperatures or longer times), other phases form and the system approaches its equilibrium state of a silicon-rich silicide (silicon-rich because there is only a thin metal film on a thick Si substrate).

This section has been devoted to silicide formation; however, studies of metal film reactions with compound semiconductors are also providing a wealth of information. The situation is complicated because of the binary nature of the semiconductor, but this complication can lead to some interesting results. For example, Pt thin films on GaAs show some features similar to Pt films on Si in that a stable PtAs$_2$ layer can be formed (*37*). The reactions are initiated by the rapid out-diffusion of Ga and, on completion, a layered structure of GaAs, PtAs$_2$, and PtGa results, with the GaAs, PtAs$_2$ interface being reasonably sharp.

In all of this work on compound formation by solid-phase reactions, the nature of the interface must be considered. A thin oxide layer, SiO$_2$ in the metal-Si systems, is nearly always present at the interface unless stringent precautions are taken. In many silicide-forming systems, a thin oxide is sufficient to seriously influence the kinetic behavior of silicide formation. The presence of a thick SiO_2 layer can actually change the phase of the silicide that is first formed. For V on Si, a silicon-rich silicide forms while for V on SiO_2 a vanadium-rich silicide is found (*38*). It is interesting to note that the vanadium-rich silicide layer shows superconducting properties with a transition temperature of 15°K.

Simple eutectic metal-semiconductor systems. We have devoted the above discussion to phase formation because it represents such a striking demonstration of low temperature reactions. There are many examples of low temperature reactions between metal and Si or between two metal layers that can occur without phase formation. We have shown in Fig. 2 that Si can diffuse in Au films at temperatures below the eutectic. Similar phenomena are found in Al-Si systems; in fact, the presence of such reactions has plagued the semiconductor industry in the formation of contacts in integrated circuits (*39*). Figure 10 shows the severe erosion that can occur on Si surfaces due to the dissolution of Si into the Al film (*40*). This condition is aggravated by the fact that the Al makes contact to the Si at only small-area, selected regions and the Si dissolves long distances into the surrounding Al film until the solubility value of Si in Al is reached at the reaction temperature.

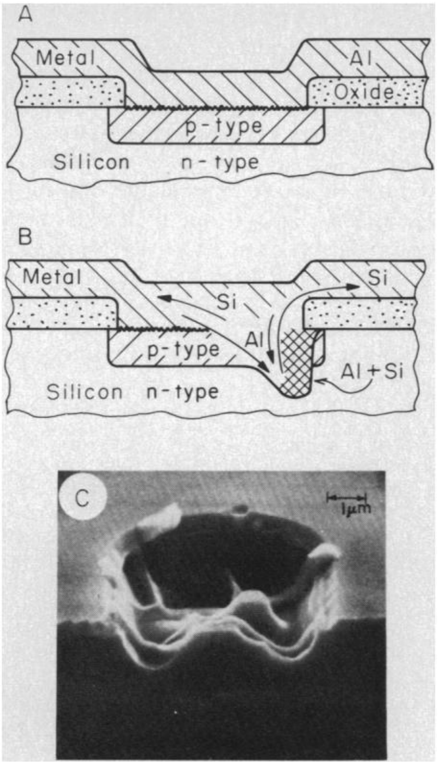
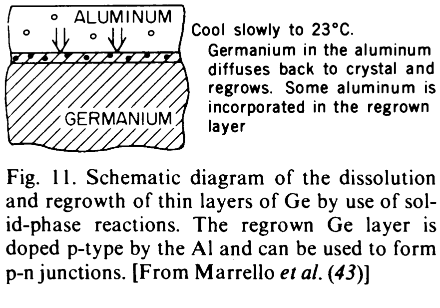


Fig. 10. Schematic diagrams and scanning electron microscope photographs of the erosion of Si that can occur when heat treating Al films are in contact with Si devices used in integrated circuits: (A) As-deposited structure with Al in contact with p-type layer of Si p-n junction; (B) after heat treatment at temperatures around 400°C solid-phase reactions between Al and Si occur; and (C) view of the Si surface after the Al layer is removed. [From Bower (*40*)]

In contact with Al films, Ge also will dissolve and migrate until the solubility value is reached at the reaction temperatures (*41*). The solubility values in the solvus curve depend strongly on temperature. As outlined in Fig. 11, this fact allows the possibility of using solid-phase reactions to grow epitaxial layers incorporating Al to form transistors (*42*) and nuclear particle detectors (*43*). Here one dissolves Ge in the Al film during the heating cycle, and then regrows the Ge on the underlying Ge crystal substrate during the cooling cycle.



Deposit thin layer of aluminum (≈1 um thick) on substrate of germanium

Heat below melting point (200-300°C). Germanium disolves into aluminum (≈1-2 atomic percent)

Cool slowly to 23°C. Germanium in the aluminum diffuses back to crystal and regrows. Some aluminum is incorporated in the regrown layer

Fig. 11. Schematic diagram of the dissolution and regrowth of thin layers of Ge by use of solid-phase reactions. The regrown Ge layer is doped p-type by the Al and can be used to form p-n junctions. [From Marrello *et al.* (*43*)]

Metal-metal reactions. The field of interdiffusion in metal-metal thin film systems is also a subject of intense study. It has been highlighted in several recent conferences and most work has been directed at understanding and characterizing the conductor metal systems used in integrated and hybrid circuits. Gold, with its resistance to corrosion and low susceptibility to electromigration, is an ideal choice as a thin film conductor system. However, there is the distinct drawback that Au does not adhere very well to dielectrics such as SiO_2. This is overcome by the introduction of a "glue" metal such as Ti or Cr between the Au and substrate. Unfortunately, Ti-Au or Cr-Au form fast corrosion couples, and to overcome this problem a third barrier, or passivating metal layer (such as Pd or Pt), is added. The interdiffusion characteristics of these multilayer metal systems have to be known, but it is only recently, with the advent of such techniques as Rutherford backscattering and Auger spectroscopy, that quantitative studies have been performed (*16*, *44*). The interactions are quite complex; however, interdiffusion between the Pd and Au has been shown to be dominated by grain boundary diffusion and defect-enhanced diffusion within the grains. The metals Pd and Au form a complete series of solid solutions and so the diffusion kinetics are not influenced by compound formation.

It is possible to elucidate the role of grain boundary and bulk diffusion effects by comparing diffusion through single crystal and polycrystalline films. For example, couples of Ag-Au can be prepared in this fashion. With single crystal layers of Ag, Au exhibits minimal diffusion for temperatures of around 200°C, as compared to marked interdiffusion in corresponding polycrystalline thin films (*45*). This comparison nicely demonstrates the role of grain boundaries in couples that form complete solid solutions.

Aluminum enjoys widespread use, more so than Au, as a thin film–conductor metallization for integrated circuits. It has the interesting propensity of forming intermetallic phases with a wide variety of other metals. This was demonstrated graphically in the electronics industry by the appearance of "purple plague" when thin film Al and Au were contacted together (*46*). The most distressing symptom of this disease was the loss of mechanical strength of the metallic bond. Aluminum and Au form the intermetallic $AuAl_2$ at relatively low temperatures with a characteristic purple color, and it is well known that intermetallic phases are often brittle. Backscattering experiments have now been carried out on both the Al-Au (*11*) and Al-Ag (*47*) thin film systems where discrete compound layers are observed to grow in a fashion very similar to that of the silicides discussed before.

Metallic thin film reactions can also be applied to study the soldering process. One of the major techniques for interaction in microelectronics is the use of solder joints with low melting points. Since joining is basically a process of interfacial reaction, a controlled reaction with the formation of ductile and highly conductive intermetallic compounds is desirable. For example, Sn with Cu forms ductile and good conducting Cu-Sn compounds. However, Cu wires are commonly soldered by Pb-Sn solders that are Pb-rich. This is because Cu reacts extremely fast with Sn but not with Pb, so Pb is used to limit the reaction so that not all the Cu is consumed and the integrity of the Cu conductor is maintained.

Thin film reactions in couples of a layer of Pb or Sn and another layer of Cu, Ag, Au, Ni, Pd, or Pt have been studied by the use of glancing angle x-ray diffraction (*48*). Intermetallic compounds have been found to form and grow near room temperature. The compound formed is the one that is rich in Pb or in Sn, for example, Pb_2Pd. The formation rates were so fast that they cannot be explained without a fast diffusion process. Indeed, noble and near-noble metals have been reported to diffuse by an interstitial mechanism in Pb and Sn (*49*).

Conclusion

We have attempted to illustrate the nature of thin film reactions with some cogent examples which have come principally from the field of integrated circuits. Our objective has been to show that the occurrence of low temperature solid-phase reactions can be analyzed by a variety of existing techniques. We hope that, as we come to an understanding of the physical nature of these films and their interfaces, correlations can be made with other physical parameters such as Schottky-barrier heights or superconducting transition temperatures.

In conclusion, therefore, we would like to emphasize that the study of solid-phase reactions in thin film systems and interface properties was prompted by the increased use of thin films in modern technology. The study of these systems was greatly facilitated by the development of three analytical concepts—depth profiling by nuclear techniques, the combination of surface analytical techniques combined with layer removal by sputtering, and glancing angle x-ray diffraction. These three, along with the more established tools of scanning electron microscopy, electron microprobe, and transmission electron microscopy, have provided pronounced new insights into the behavior of thin film systems.

The development of analytical tools with capability for depth microscopy on a submicron scale offers a unique opportunity for the study of low temperature reactions. Although we have stressed the study of thin film systems, these same tools have been used in studies of oxidation and corrosion, ion implantation in metals and semiconductors, and front wall degradation in fusion reactors.

References and Notes

1. J. W. M. Dumond and J. P. Youtz, *Phys. Rev.* **48**, 703 (1935).
2. ———, *J. Appl. Phys.* **11**, 357 (1940).
3. H. E. Cook and J. E. Hilliard, *ibid.* **40**, 2191 (1969); E. M. Philofsky and J. E. Hillard, *ibid.*, p. 2198.
4. K. N. Tu and B. S. Berry, *ibid.* **43**, 3283 (1972).
5. C. Weaver and L. C. Brown, *Philos. Mag.* **7**, 1 (1962); C. Weaver and D. T. Parkinson, *ibid.* **22**, 377 (1970).
6. K. N. Tu, *Acta Metall.* **21**, 347 (1973).
7. K. Nakamura, J. W. Mayer, M-A. Nicolet, C. A. Evans, R. J. Blattner, *J. Appl. Phys.*, in preparation.
8. K. Nakamura and S. S. Lau, unpublished result.
9. S. Herd, P. Chaudhari, M. H. Brodsky, *J. Non-Cryst. Solids* **7**, 309 (1972); G. Ottaviani, D. Sigurd, V. Marrello, J. W. Mayer, J. O. McCaldin, *J. Appl. Phys.* **45**, 1730 (1974).
10. M. P. Lepselter and J. M. Andrews, in *Ohmic Contacts to Semiconductors*, B. Schwartz, Ed. (Electrochemical Society, New York, 1969), p. 169; J. A. Borders and S. T. Picraux, *Proc. IEEE* **62**, 1224 (1974).
11. S. U. Campisano, G. Foti, E. Rimini, S. S. Lau, J. W. Mayer, *Philos. Mag.* **31**, 903 (1975).
12. K. N. Tu and D. A. Chance, *J. Appl. Phys.* **46**, 3229 (1975).
13. W. J. DeBonte and J. M. Poate, *Thin Solid Films* **25**, 441 (1975).
14. D. Gupta, *J. Appl. Phys.* **44**, 4455 (1973).
15. R. W. Bower and J. W. Mayer, *Appl. Phys. Lett.* **20**, 359 (1972); L. D. Locker and C. D. Capio, *J. Appl. Phys.* **44**, 4366 (1973).
16. J. M. Poate, P. A. Turner, W. J. DeBonte, J. Yahalom, *J. Appl. Phys.*, in press.
17. H. Sankur, J. O. McCaldin, J. Devaney, *Appl. Phys. Lett.* **22**, 641 (1973).
18. M-A. Nicolet, J. W. Mayer, I. V. Mitchell, *Science* **177**, 841 (1972).
19. J. M. Morabito, *Thin Solid Films* **19**, 21 (1973).
20. W. K. Chu, J. W. Mayer, M-A. Nicolet, T. M. Buck, G. Amsel, F. Eisen, *ibid.* **17**, 1 (1973).
21. J. A. Cairns, A. D. Marwick, I. V. Mitchell, *ibid.* **19**, 91 (1973).
22. G. Amsel, T. P. Nadai, E. D'Artemare, D. David, E. Girard, J. Moulin, *Nucl. Instrum. Methods* **92**, 481 (1971).
23. C. C. Chang, *Surf. Sci.* **25**, 53 (1971).
24. C. A. Evans and J. P. Pensler, *Anal. Chem.* **42**, 1060 (1970).
25. D. P. Smith, *Surf. Sci.* **25**, 171 (1971); D. J. Ball, T. M. Buck, D. MacNair, G. H. Wheatley, *ibid.* **30**, 69 (1972).
26. K. N. Tu, W. K. Chu, J. W. Mayer, *Thin Solid Films* **25**, 403 (1975).
27. J. Ziegler and W. K. Chu, *At. Data Nucl. Data Tables* **13**, 463 (1974).
28. W. K. Chu, M-A. Nicolet, J. W. Mayer, C. A. Evans, *Anal. Chem.* **46**, 2136 (1974).
29. R. Feder and B. S. Berry, *J. Appl. Phys.* **43**, 3283 (1972).
30. M. H. Read and D. H. Hansler, *Thin Solid Films* **10**, 123 (1972).
31. L. R. Testardi, R. L. Meek, J. M. Poate, W. A. Royer, A. R. Storm, J. H. Wernick, *Phys. Rev. B* **11**, 4304 (1975).
32. S. S. Lau, W. K. Chu, J. W. Mayer, K. N. Tu, *Thin Solid Films* **23**, 205 (1974).
33. J. W. Mayer and K. N. Tu, *J. Vac. Sci. Technol.* **11**, 86 (1974).
34. K. N. Tu, *Appl. Phys. Lett.* **27**, 221 (1975).
35. E. O. Kirkendall, *Trans. Am. Inst. Min. Metall. Pet. Engl.* **147**, 104 (1942).
36. W. K. Chu, H. Krautle, J. W. Mayer, H. Muller, M-A. Nicolet, K. N. Tu, *Appl. Phys. Lett.* **25**, 454 (1974).
37. A. K. Sinha and J. M. Poate, *ibid.* **23**, 666 (1973).
38. K. N. Tu, J. F. Ziegler, C. J. Kircher, *ibid.*, p. 493.
39. J. O. McCaldin, *J. Vac. Sci. Technol.* **11**, 990 (1974).
40. R. W. Bower, *Appl. Phys. Lett.* **23**, 99 (1973).
41. J. M. Caywood, *Metall. Trans.* **4**, 735 (1973).
42. J. O. McCaldin and A. Fern, *Proc. IEEE* **60**, 1018 (1972).
43. V. Marrello, T. A. McMath, J. W. Mayer, I. L. Fowler, *Nucl. Instrum. Methods* **108**, 93 (1973).
44. P. M. Hall, J. M. Morabito, J. M. Poate, in preparation.
45. K. N. Tu and R. Rosenberg, *Thin Solid Films* **13**, 163 (1972).
46. E. Philofsky, *Solid State Electron.* **13**, 1391 (1970).
47. S. T. Picraux, *Jpn. J. Appl. Phys.* (Suppl. 2, Pt. 1) (1974), p. 657.
48. K. N. Tu and R. Rosenberg, *ibid.*, p. 633.
49. W. Warburton and D. Turnbull, *Thin Solid Films* **25**, 71 (1975).
50. We acknowledge the contributions of our colleagues at Bell Laboratories, IBM–Watson Research Center, and Caltech to many of the concepts presented here. The Caltech work was supported by grants from the Ford Motor Foundation and the Office of Naval Research (L. Cooper). The IBM work was supported in part by ARPA contract F19628-74-C-0077.

Membrane Electrode Probes for Biological Systems

New sensors expand measurement horizons.

G. A. Rechnitz

Scientific progress is limited not only by the rate of generation of new ideas but also by the state of development of appropriate experimental tools and techniques. As a result, there is a constant interplay between theoretical advances and the development of new instrumentation, with one or the other leading at any particular time. Since most scientific hypotheses cannot be tested without experimentation, measurement capabilities and associated instrumentation provide a common ground for theoretical and experimental scientists and serve as a powerful integrating force between scientific specialties.

At the present time, it seems that conceptual advances in the biological and biochemical sciences have temporarily outrun our ability to perform unambiguous measurements in real systems with regard to the nature, concentration, and time-dependent fate of chemical species on the cellular and molecular level. Certainly, much of the experimental work being carried out now employs simplified "model" systems or relies upon highly indirect observations.

This situation could be changed through the development of new instrumental techniques designed to permit selective and nondestructive measurements to be made in complex systems on a direct and, preferably, continuous basis. There is reason to believe that several membrane electrode