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The Preparation and Properties of Silicon Nitride Coatings
on Copper and Copper Alloys

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Report Written by: Sylvain Audisio and Henry Leidheiser, Jr.

Center for Surface and Coatings Research
Lehigh University
Bethlehem, Pennsylvania 18015

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SUMMARY

Silicon nitride was deposited on copper substrates at room temperature by a reactive sputtering technique. The coatings, in the thickness range 500-1500 Å., were amorphous, transparent, and had glass-like smoothness. They were tightly adherent to the substrate. Infrared analysis indicated the coatings were pure silicon nitride when precautions were taken to eliminate oxygen and water from the system. The coatings exhibited dielectric constants of 8-11 with a dissipation factor of 10^{-2} at 1000 cycles/sec. The ductility approached 1% as measured on a copper substrate. The coatings appreciably reduced the charge passing across the metal/electrolyte interface when the coated samples were anodically treated in sodium hydroxide, sulfuric acid, and phosphoric acid. The coatings provided good resistance to attack of the copper surface in ammonium hydroxide and sodium hypochlorite; provided moderate protection in concentrated acids; mediocre protection in sodium thiosulfate and sodium sulfide solutions; and very little protection in concentrated nitric acid.

INTRODUCTION

Preliminary discussions with representatives of the International Copper Research Association in August 1969 indicated a growing need within the industry for new kinds of coatings which have advantageous electrical properties and useful tarnish-resistant and corrosion-resistant properties. Lehigh University indicated its willingness to explore the preparation and properties of a candidate coating, silicon nitride, after carrying out a few tests on samples prepared by an electronics laboratory which was examining silicon nitride as a potential coating for electronic components. This report summarizes findings on the preparation and properties of silicon nitride coatings on copper substrates.

The work reported herein was initiated on April 1, 1970 and includes data obtained through March 31, 1971. A hiatus in the work is planned to allow the monitoring committee of INCRA to evaluate the findings in order to determine if silicon nitride coatings have applications useful to the copper industry.

BACKGROUND INFORMATION

Silicon nitride has very attractive chemical and physical properties which have encouraged its use as a coating material for microelectronic devices. The properties of silicon nitride coatings on semiconductor substrates are summarized in Table I.

The three major methods for depositing silicon nitride on high-melting substrates are (1) chemical vapor deposition, (2) reactive sputtering, and (3) rf glow discharge. Comments on these three methods are given in the following paragraphs.

Chemical Vapor Deposition of silicon nitride is carried out by reacting a silicon compound such as SiH_4 , SiCl_4 , or SiBr_4 with nitrogen or ammonia at temperatures above 800°C . This method is not attractive for use with copper alloys because the high temperature required will lead to changes in the metallurgical structure and consequent changes in physical properties.

Reactive Sputtering is a technique which involves the sputtering of silicon in a nitrogen plasma. The method has the advantage that it does not require heating of the substrate because the energy is supplied by the discharge. The chief shortcoming of the method is that precautions must be taken to eliminate oxygen or oxygen-containing compounds from the system in order to avoid the codeposition of silicon dioxide. It should be pointed out, however, that insufficient evidence is available to determine if contamination of the coating with co-deposited silicon dioxide is necessarily bad when the coatings are applied to copper.

Radiofrequency Glow Discharge. Silicon nitride is deposited by reacting ammonia and SiH_4 in a radiofrequency glow discharge. The apparatus is very simple and requires no internal electrodes, targets, or water-cooling facilities. The chemical reactions

TABLE I

The Properties of Silicon Nitride Coatings Formed by Three Methods

	Chemical Vapor Deposition	Reactive Sputtering	RF Glow Discharge
Temperature of substrate	800°C	400°C	400°C
Structure of deposit	Amorphous	Amorphous	Amorphous
SiN Infrared Absorption Band	10-12 μ (14)	12 μ (20)	12.1 μ (29) 11.4-12.1 μ (28)
Index of Refraction	1.9-2.20 (16) 2-2.06 (14)	2.2 (18)	-----
Dielectric Constant	6.2 (2)	6.2 to 8.5 (20) 10 (18) 6.4 (19)	7 to 11 (29) 7 to 14 (28) Changes with the concentration of silane and with the temperature; increases with increase in silane concn., increases with decrease in temperature (30)
Breakdown Voltage	3.9 x 10 ⁶ to 9.5 x 10 ⁶ V/cm (16) 10 ⁷ V/cm (14) 0.5 x 10 ⁷ to 1 x 10 ⁷ V/cm (6)	5 x 10 ⁶ V/cm (20) 10 ⁷ V/cm 4 to 10 x 10 ⁶ V/cm (19)	6 x 10 ⁶ v/cm to 1 x 10 ⁶ V/cm when rate of silane goes from 9% to 50% (29)
Electric Resistivity	10 ⁸ - 10 ¹⁰ Ω cm (9) 1 x 10 ¹⁵ to 2 x 10 ¹³ Ω cm (2)	5 x 10 ¹³ to 2 x 10 ¹⁴ Ω cm (19)	8 x 10 ¹⁶ Ω cm to 5 x 10 ¹² Ω cm when rate of silane goes from 9% to 50% (29)
Thermal Expansion	2.5-3.5 x 10 ⁻⁶ deg ⁻¹ (1)	2.5 x 10 ⁻⁶ deg ⁻¹ (18)	-----
Growth Rate	Increases with the percentage of silane or SiCl ₄ , and with temperature Ex: 712°C SiH ₄ /NH ₃ = 0.150 = 1000 Å/min (9)	20 Å/min to 150 Å/min when power density increases from 1 to 5 W/cm ² (20)	Variable with the rate of silane in the gas; 180 Å/min at 50% silane; 35 Å/min at 10% silane (27, 29)
Etch Rate	Decreases when the % of silane or SiCl ₄ increases in mixture; when temperature of deposition is increased, etch rate decreases Ex: in 48% HF, Etch = 75-100 Å/min (16)	In 1/7 = HF/NH ₄ F solution the etch rate is a function of the power density 240 Å/min to 10 Å/min when power density goes from 1 to 5 W/cm ² (20)	In 1/8 = HF/NH ₄ F etch rate is function of the silane concentration 50 Å/min to 20 Å/min (29)

which take place in the glow discharge are very complex and oxygen contamination is a problem.

Several other techniques have also been used to form silicon nitride coatings, but these methods have shortcomings which do not make them suitable candidates for use with copper substrates.

A summary is given in Table I of the properties of silicon nitride coatings formed by the three major methods.

Reactive sputtering was chosen over radiofrequency glow discharge because of its simplicity, the ease in changing experimental variables, and because preliminary experiments indicated high quality coatings were obtained. The three important steps which govern the formation of silicon nitride coatings by reactive sputtering are : (1) sputtering of silicon atoms from the cathode, (2) activation of the sputtered silicon atoms and interaction with nitrogen species, and (3) condensation of the silicon-nitrogen compound on the anode. The glow discharge ionizes the nitrogen which is then accelerated by the electric field to the cathode. The impact is so energetic that silicon atoms are sputtered from the surface. Reactions take place in the gas phase, and perhaps on the substrate as well, with the formation of silicon nitride on the copper anode.

In order to attain a high rate of deposition of silicon nitride, it is important to maximize the number of silicon atoms permanently sputtered from the cathode. The number of atoms permanently sputtered from the surface is the difference between those sputtered and those which recondense on the silicon as a consequence of collision with gaseous species. Thus the gas pressure must be sufficiently high to maintain the discharge and yet low enough to reduce sufficiently the number of collisions in the gas phase. The voltage between the cathode and anode must be high enough to maintain the

glow discharge yet low enough to avoid sparking. The cathode-anode distance must be optimized to maximize the rate of deposition of silicon nitride and yet avoid sparking. The important experimental variables are thus the cathode-anode spacing (d), the gas pressure (p), and the fraction of sputtered atoms which are permanently removed from the silicon cathode (S). For the range of experimental conditions used in this study, S is approximately inversely proportional to the product of d and p : $S \cong 1/dp$.

EXPERIMENTAL METHOD

Many preliminary experimental designs led to the adoption of the experimental arrangement shown schematically in Figure 1. After achieving a vacuum of 10^{-6} mm., ultrapure nitrogen is flowed through the system at a pressure of 0.2-0.3 mm. A DC glow discharge is maintained between a water-cooled silicon cathode and a copper anode arranged at 90° to the cathode by application of a potential of 1500-2000 v. The current passed between the anode and the cathode is of the order of 3 milliamp./cm.² under the conditions used. The copper substrate, on which the silicon nitride coatings is desired, is placed in the gas stream, in a parallel position with the silicon cathode.

Both electrodes were protected on their periphery by quartz sleeves. If this precaution was not observed, sparking occurred at the edges with rapid deterioration of the electrodes and consequent inability to maintain a good discharge without sparking. In order to obtain high quality coatings it was essential to avoid sparking when the voltage was first applied by gradually increasing the potential until the glow discharge was observed. The cathode-substrate spacing finally adopted was 2.5 cm.

The copper substrate in the form of a square sheet, 1.5 x 1.5 x 0.1 cm., was surfaced before each deposition either by electrolytic polishing in phosphoric acid or by metallographic polishing. No difference was observed between these two types of surfacing procedures.

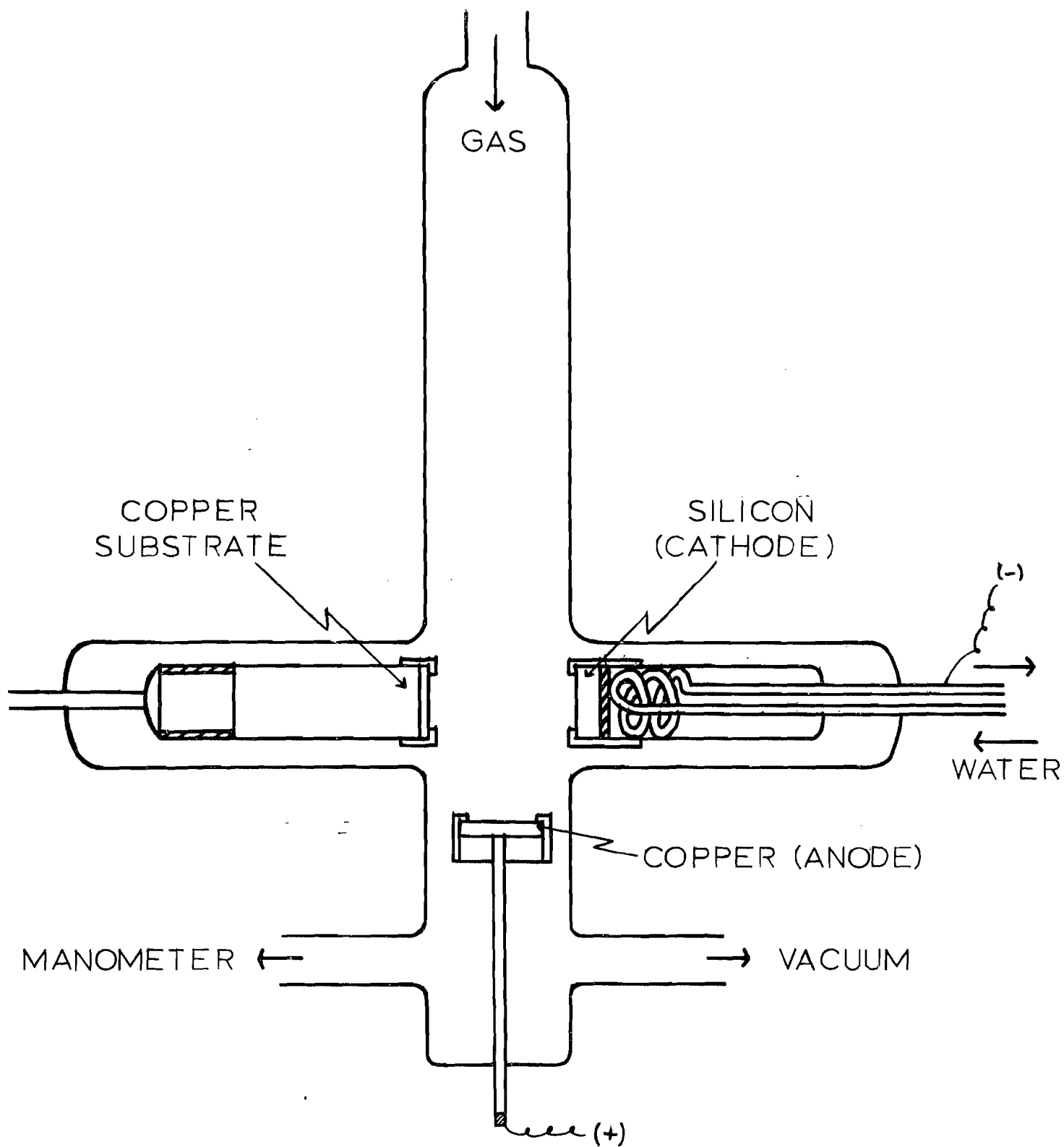


Figure 1. Schematic diagram of the apparatus used for the deposition of silicon nitride coatings by reactive sputtering.

EXPERIMENTAL RESULTS

It was the original plan of this research to determine the composition of the coating and a limited number of physical properties as a function of the conditions under which the coating was prepared. It was of special interest to determine the effect of rate of formation on the properties of the coating. This approach assumed that the research would be supported for a minimum of two years and that the second year would be devoted to optimizing those properties or parameters of preparation of greatest interest to INCRA based on the information generated during the first year. Under pressure from the scientific monitors, this approach was abandoned in order to obtain quantitative information about a greater number of properties on samples prepared under a fixed set of experimental conditions. These comments are made to justify the fact that property measurements have been made on samples prepared under low growth-rate conditions with full recognition that the rates of formation are far below those which make the process practical from a processing standpoint. It is not known at the present time whether samples prepared at higher growth rates would lead to coatings with inferior or superior properties.

All samples on which property measurements were made were prepared under the following experimental conditions: Nitrogen gas pressure - 0.2-0.3 mm. ; cathode-substrate spacing - 2.5 cm. ; potential between cathode and anode - 1500-2000 v. ; current - 3 milliamp./cm.² Unless otherwise stated, the coatings were 1000-1200 A. in thickness and the rate of coating growth was 15 A./min.

Rate of Coating Growth. A computer program was developed to calculate film thickness from readings obtained with an ellipsometer. This instrument measures the

changes in optical properties of monochromatic polarized light upon reflection from a surface covered with a thin film of a transparent or semi-transparent material with refractive index different from that of the substrate. Once a calibration curve was obtained, qualitative estimates of the coating thickness could be obtained by noting the interference color generated by the coating.

Figure 2 shows the rate of film growth under the slow-growth conditions adopted. In the early stages the rate is approximately 15 A./min.

Qualitatively, the rate of coating growth increased with increase in anode-cathode potential, with increase in current, and with decrease in anode-substrate spacing.

Composition of the Coating. Since the coatings did not give suitable X-ray diffraction patterns, it was necessary to utilize another method for determining the composition of the coating. Infrared absorption appeared appropriate.

Highly polished silicon or germanium substrates were substituted for the copper during coating formation and films approximately 1500 A. in thickness were deposited. Silicon and germanium substrates were used because of their transparency in the spectral region of interest.

During the early stages of the development of the coating method, it was observed that absorptions characteristic of silicon dioxide were obtained along with those of silicon nitride. The preparation method was then modified to minimize oxygen and water contamination in the system. The following precautions eliminated silicon dioxide contamination: (1) the use of ultrapure nitrogen, (2) pumping the system down to 10^{-6} mm. before admission of nitrogen, (3) flushing the system with nitrogen before starting the experiment, and (4) maintaining the system under vacuum when not in use.

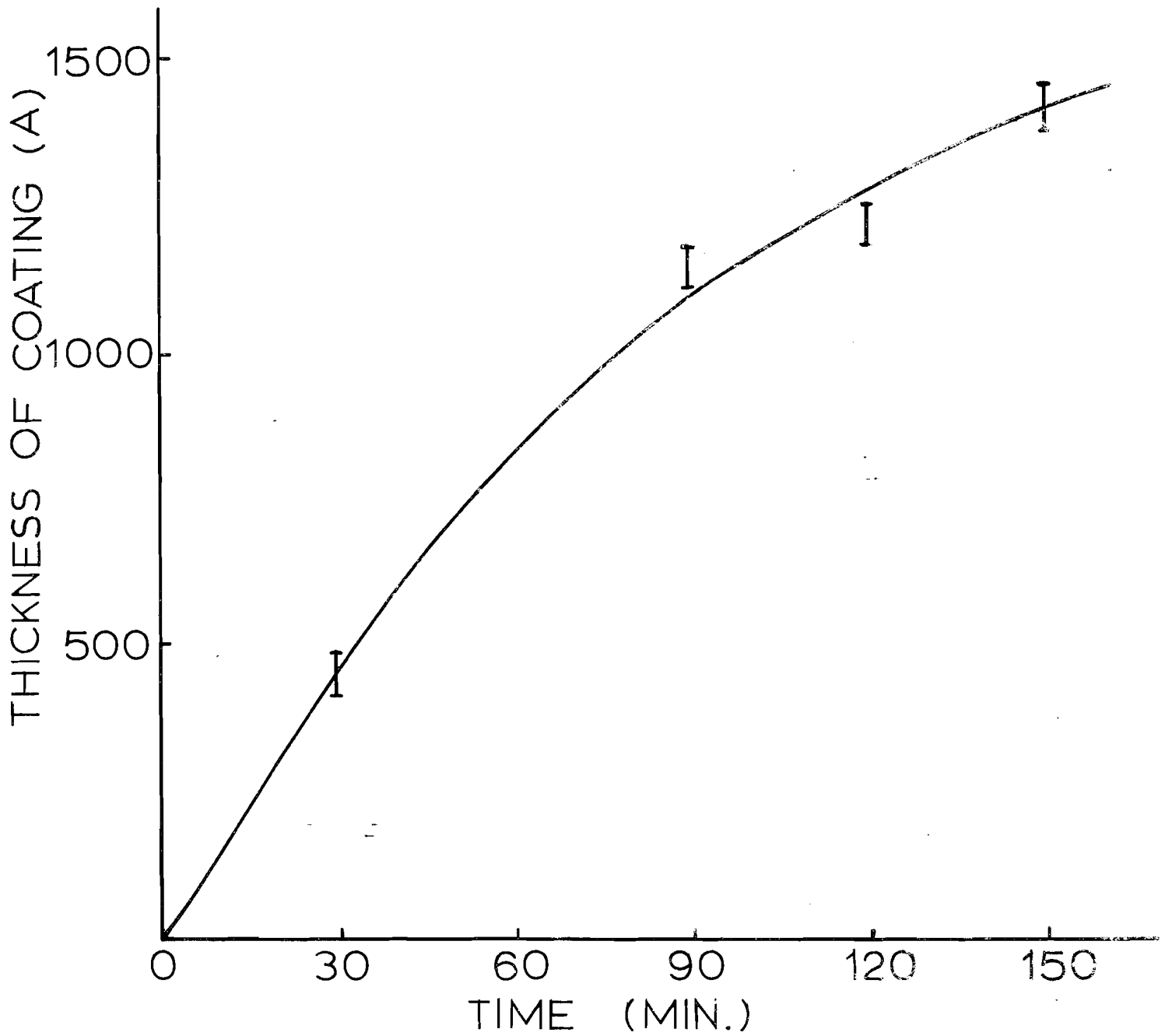


Figure 2. Rate of growth of silicon nitride coatings under the slow-growth conditions used.

A typical infrared absorption spectrum of the silicon nitride coating is given in Figure 3. The broad absorption band centered at 900 cm.^{-1} is characteristic of silicon nitride. The absorption band centered at 2200 cm.^{-1} has been attributed to a silicon-nitrogen triple bond and may indicate a lack of stoichiometry in the coating.

Adherence. All films deposited in this study were very adherent to the substrate as judged by the fact that harsh rubbing with non-abrasive papers or cloths had no effect on the coating. Samples could be severely bent without macroscopic separation of the coating from the substrate. Quantitative measurements of adherence were not performed.

Macroscopic and Microscopic Features of Coating. The films were smooth and mirrored the smoothness of the substrate. They imparted slight color presumably as a consequence of interference between light reflected from the silicon nitride-air interface and the copper-silicon nitride interface. Films, 300-400 A. in thickness, were reddish to brown in color, and films, 1000-2000 A. in thickness, were yellow to gold in color.

The coating appeared transparent and structureless under the microscope and the grain boundaries of the substrate were readily visible on electropolished specimens. See Figure 4 as an example of the featureless nature of the coating when examined at 800X magnification.

Electrical Properties of the Coating. The dielectric constant of 8 films ranging in thickness from 500 to 1000 A. was determined at 1,000 cycles/sec. Two different systems were used: (1) copper-silicon nitride-gold, and (2) copper-silicon nitride-mercury. The gold was applied to the silicon nitride coating by evaporation in vacuum.

The dielectric constant of the coatings ranged from 8 to 11 in the different samples. Literature values, as summarized in Table I range from 6 to 14. It is likely that the

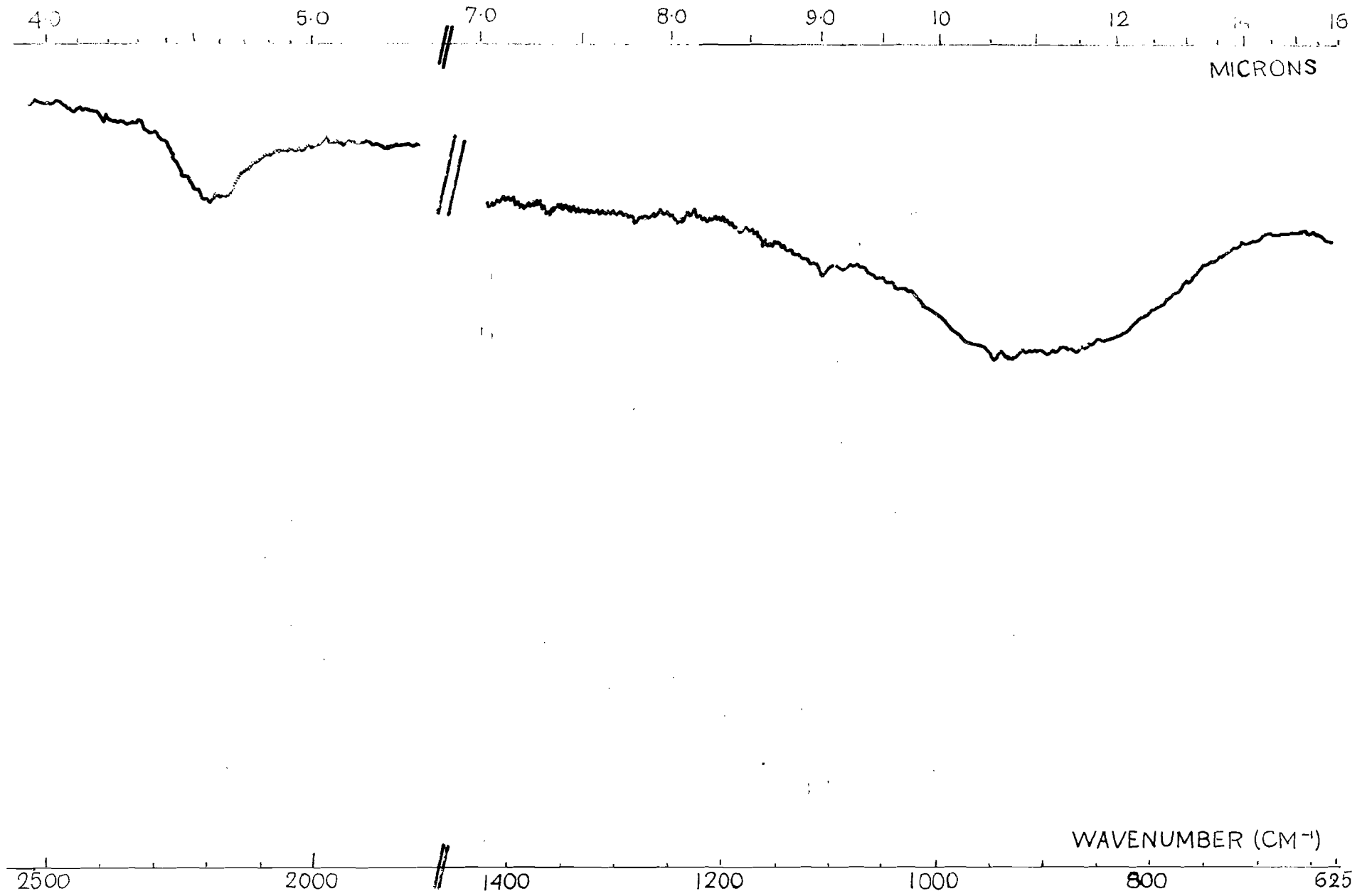


Figure 3. Infrared absorption spectrum of silicon nitride coating formed on a germanium substrate.

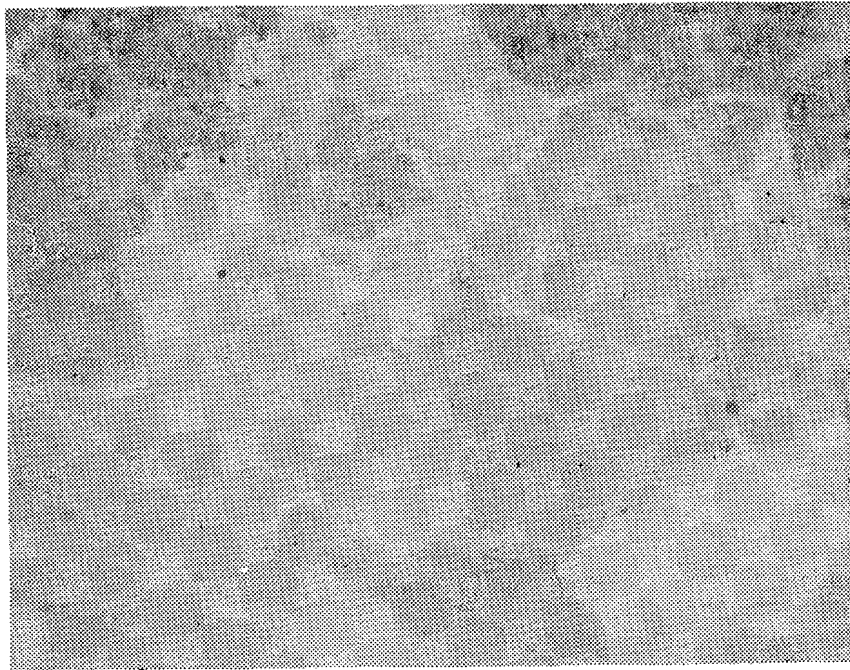


Figure 4: Featureless nature of a 1000 Å. thick coating of silicon nitride on electropolished copper. X800

dielectric constant is intimately associated with the structure and stoichiometry of the coatings, but no efforts were made to make such a correlation since this objective did not appear to warrant the effort at this stage of the work. The possible cause for the high dielectric constant of the coatings is the increase in molecular and dipole polarizabilities due to the amorphous structure or the presence of shallow impurity levels causing high electronic polarizability.

The dissipation factor at 1,000 cycles/sec. was determined to be less than 10^{-2} .

A very important property of silicon nitride coatings from the standpoint of the copper industry is the ability of the coating to limit charge movement across the copper-environment interface, either for electrical resistance purposes or for corrosion prevention. It was decided that the most appropriate method for characterizing simultaneously the electrical and corrosion resistant properties of the film was by means of the behavior of the copper under an applied potential while immersed in a conducting medium. The simplest means for determining this property is to monitor the current passing across the copper-silicon nitride-electrolyte interface as a function of potential. Such measurements yield a so-called polarization curve. Typical polarization curves are given in Figures 5-7. All potentials are given with respect to a mercurous sulfate reference electrode.

Figure 5 compares the polarization curves obtained on pure copper (solid line) and on silicon nitride-coated copper (broken line) in 1N sodium hydroxide. The magnitude of the current flowing at the same potential was significantly less in the case of the silicon nitride-coated copper than with uncoated copper in both the anodic and cathodic directions. The very high anodic current at small anodic potential observed in the case of copper was not observed with the silicon nitride-coated copper.

Figure 6 compares the polarization curves obtained with pure copper (curve 1) with the polarization curves of a silicon nitride-coated sample (curve 2) in 2N phosphoric acid. The amount of current flowing at equivalent potentials is approximately 2 orders of magnitude less in the case of the silicon nitride-coated copper. Curve 3 represents a second run on the same sample used to give curve 2. It will be noted that the plateau region in curve 3 has the same value as the highest current used in obtaining curve 2. Deterioration of the coating apparently occurs at high anodic currents.

Figure 7 gives the polarization curves obtained in 2N sulfuric acid. Curve 1 is for uncoated copper, curve 2 is for silicon nitride-coated copper, and curve 3 is for a sample previously polarized anodically in phosphoric acid. The lower current passed by the "phosphated" silicon nitride sample suggests that the coating has some porosity and that prior treatment in phosphoric acid reduces the porosity by precipitation of copper phosphate in the pores.

These results are encouraging and lend support for the view that the electrical properties of the coating are such as to restrict the flow of charge through the coating. The localized nature of the attack of the copper upon anodic treatment suggests that defects in the coating are largely responsible for charge movement through the coating.

Corrosion Resistance. Three silicon nitride-coated samples were exposed at room temperature to a number of aqueous corrosive environments in separate experiments. In each case a 0.5 cm.² section in the center of the coated sample was isolated by masking off the remainder of the surface with a proprietary resistant lacquer. All three samples gave essentially identical results so that the behavior appears typical of coatings made under the standard conditions adopted. Control samples of electrolytically polished copper were attacked immediately or within a short time in the same

cathodic \rightarrow \times anodic

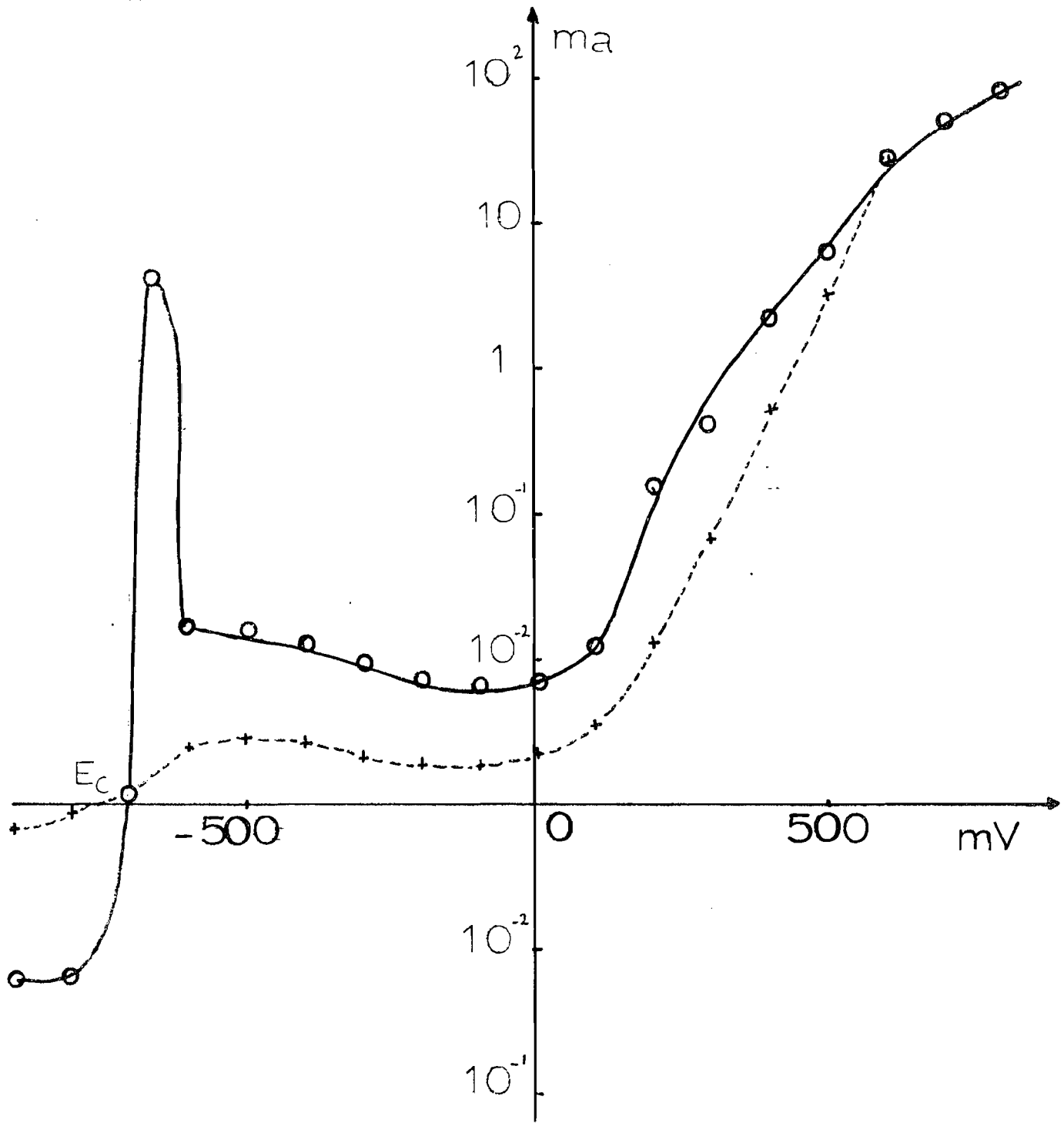


Figure 5. Polarization curves of copper (solid line) and silicon nitride-coated copper (broken line) in 1N sodium hydroxide.

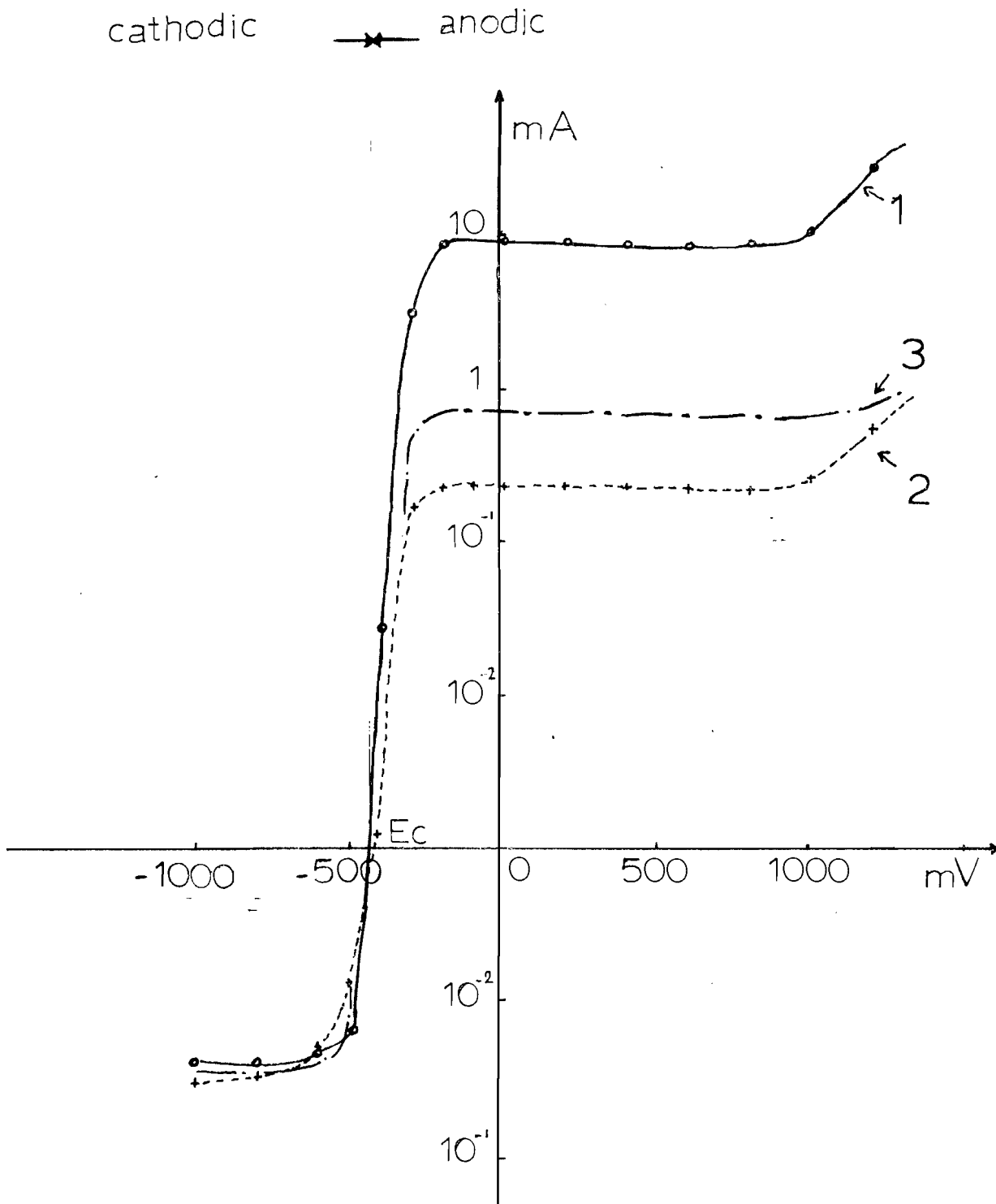


Figure 6. Polarization curves of pure copper (curve 1) and silicon nitride-coated copper (curve 2) in 2N phosphoric acid. Curve 3 is a second polarization curve on the same silicon nitride-coated sample. Note that current plateau is at the same position as the highest current used in determining curve 2.

cathodic ← x → anodic

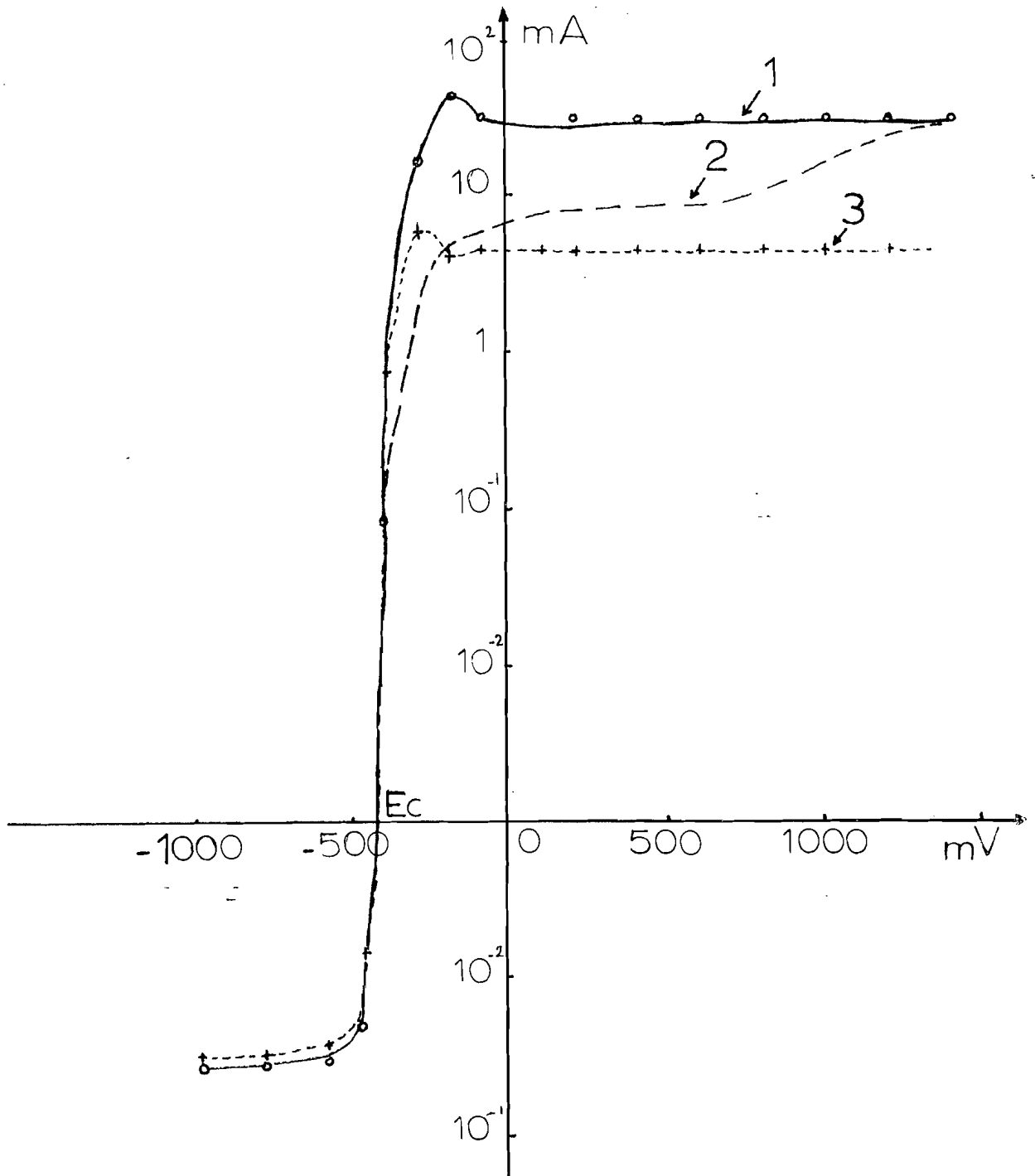


Figure 7. Polarization curves of pure copper (curve 1) and silicon nitride-coated copper in 2N sulfuric acid. Curve 3 is a polarization curve after the silicon nitride-coated sample was polarized anodically in 2N phosphoric acid. The lower current observed with the "phosphated" copper suggests that pores in the coating were sealed.

environments. The results of these experiments are summarized in Table II. Attack of the coated samples was first visible as local separation of the deposit from the substrate followed by lateral attack along the copper-silicon nitride interface with subsequent buckling of the coating.

TABLE II

Behavior of 1000 A. -Thick Silicon Nitride Coatings on Electrolytically Polished Copper Substrates upon Exposure to Corrosive Environments

<u>Corrosive Environment</u>	<u>Observed Behavior</u>
Phosphoric acid, concd.	First attack on the coating noted after 24 hours
Sulfuric acid, concd.	First attack on the coating noted after 24 hours
Nitric acid, concd.	First deterioration of the coating noted in 5 minutes
Nitric acid, 10%	Samples resisted attack for 3 hours
Ammonium hydroxide, concd.	No observable deterioration of the coating within 24 hours
Sodium hypochlorite, concd.	No observable deterioration of the coating within 24 hours
Sodium thiosulfate, 1M	First attack visible after 2 hours
Sodium sulfide, 0.1M	First attack visible after 2 hours with buckling of coating and darkening of the copper

Copper samples coated in the normal way and consisting of a coated area plus an uncoated area around the edge which was protected by the sleeve during silicon nitride deposition, were electrolyzed anodically in 70% phosphoric acid. The uncoated area became electropolished during this operation whereas the silicon nitride-coated area was completely unattacked as judged by the naked eye and by examination at magnifications

up to 800X. The silicon nitride thus afforded complete protection to the underlying copper during this electrolytic treatment and no undercutting of the coating was detected. This experiment was repeated several times during the course of the research with identical results.

Mechanical Properties of the Coating. Qualitative tests involving severe bending of the silicon nitride-coated samples indicated that the coatings had ductility and that sharp bends did not cause the deposit to flake from the surface. Quantitative experiments were then performed at the urging of INCRA.

The copper tensile test samples used in this study are shown in Figure 8. After metallographic polishing, they were coated in the gauge area on one side with a 1200-A. thick coating of silicon nitride in the apparatus shown in Figure 1. The samples were strained on an Instron Universal Testing Machine at a crosshead speed of 0.02 inches/min. The stress-strain curves were recorded on an X-Y recorder. The mechanical characteristics of the copper were found to be:

Yield strength at 0.2% strain - - - - - 25,400 psi
Ultimate tensile strength - - - - - 32,300 psi

In order to determine the mechanical behavior of the coating, axial tensile loads were applied in successive elongation steps of 0.3%, 0.5%, 0.7%, and 1.0%. After each degree of elongation, the sample was examined microscopically for indications of fracture in the coating. No cracks were detected on samples strained 0.3%, 0.5%, and 0.7%. At 1% elongation, however, short cracks largely at right angles to the loading axis were detected as shown in Figure 9. The cracks were readily identifiable by the interference fringes which occurred in areas adjoining the cracks. It is hypothesized that the coating separated from the substrate over a local area such that the silicon nitride formed an angle with the surface.

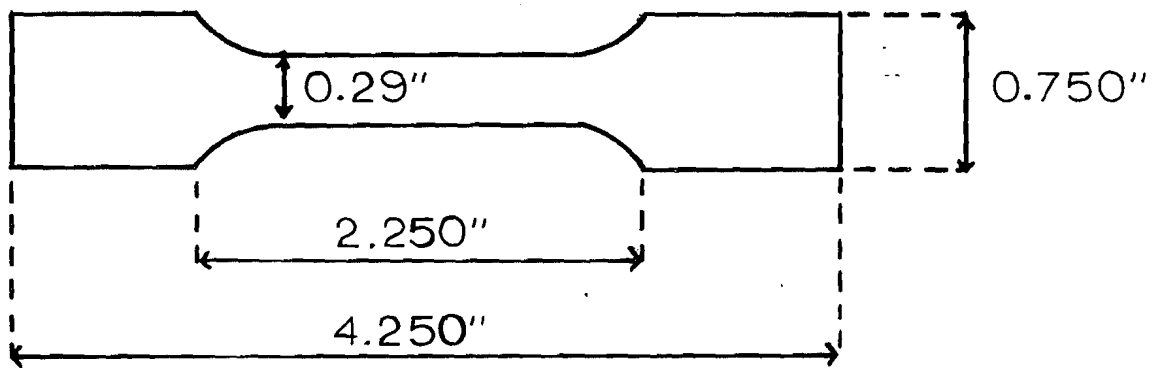


Figure 8. Copper tensile test specimen used in determining the ductility of silicon nitride coatings on copper.

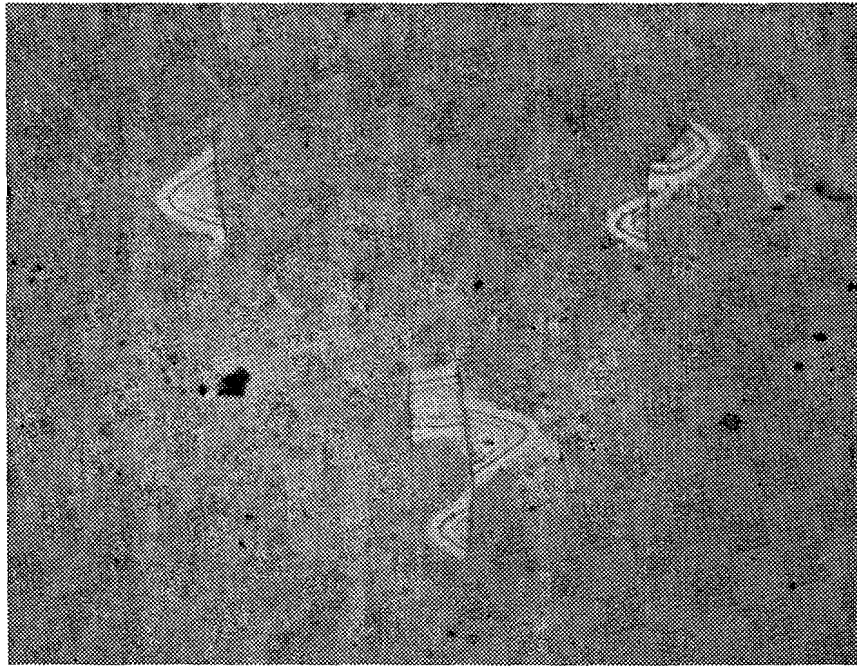


Figure 9: Photomicrograph of silicon nitride-coated copper strained 1% in tension. Cracks are readily identified by interference fringes adjoining crack. X800

DISCUSSION

The research done to date is exploratory in nature. It suffers under the handicap that the original emphasis on maximizing the rate of formation of the coating was altered as this phase was in progress to an emphasis on properties of the coating under a fixed set of experimental conditions. Each property measurement involved considerable time for generating specimens and for assembling or modifying apparatus. It was necessary to utilize specimens formed at low-growth rates because problems associated with sparking were encountered at high-growth rates and these problems were not adequately solved before the investigators were urged to obtain information on properties. Progress was being made through modifications in specimen holder design.

The chief question unanswered by this work is how are the properties of the coating related to the conditions of preparation. All data summarized in this report were obtained on coatings prepared by reactive sputtering using a DC glow discharge and experimental conditions such that the growth rate was approximately 15 A./minute. It is not known if coatings with superior or inferior properties would be obtained if higher growth rates were utilized. It is also not known whether there would be an improvement in properties if rf sputtering, rather than DC sputtering, had been adopted.

This work adequately shows that silicon nitride can be routinely deposited on copper substrates by a reactive sputtering technique in which the copper substrate is maintained at room temperature. No problems have been encountered with adherence of the coating to copper or with macroscopic defects in the coating. The coatings were crack-free and gross-defect free.

It does appear, however, that 1000 A.-thick coatings were porous to electrolytes

as judged from the fact that the coatings passed appreciable current when subjected to an applied potential in media such as sulfuric acid, phosphoric acid, and sodium hydroxide. The lack of complete protection of the coating to copper in corrosive environments over long periods is additional evidence that the coatings did not prevent electrolyte penetration to the copper substrate. Nonetheless, the silicon nitride coating did reduce greatly the rate of anodic copper dissolution and did afford short-term protection in even the most aggressive environments.

It is possible that the assumed porosity of the silicon nitride coatings may be controllable through modification in the rate or method of formation or through a post-treatment such as heat treatment. One interesting fact generated by this study is that prior anodic treatment in a phosphoric acid electrolyte reduced the current which passed through the coating under an applied potential when the sample was treated anodically in sulfuric acid. See Figure 7. Presumably, copper phosphate sealed some of the defects in the coating.

In agreement with other investigators, the coatings did not yield diffraction patterns on X-ray examination. The coatings are thus considered to be amorphous using the absence of a crystalline diffraction pattern as the criterion.

Ceramic coatings in general have very poor ductility and readily fracture at low strains. The silicon nitride coatings formed in this study tolerated strains below 1% without apparent fracture as judged by microscopic examination. At 1% strain, local fracture of the coating was visible as shown for example in Figure 9.

The chief application of silicon nitride coatings in the copper industry appears to be as a protective coating on decorative panels for indoor or outdoor use where adherence, abrasion resistance, and resistance to mildly corrosive environments are

vital. Retention of the color of the substrate is possible with thin coatings up to several hundred Angstroms in thickness and color modification is possible with control of the thickness in the 500-1500 A. range. The coating of small parts in a continuous process appears feasible using D_c sputtering from silicon cathodes arranged in the proper geometry along the length of the reaction chamber. The coating of very large panels and parts with complex shapes is probably more feasible using a glow discharge in a reactive environment containing silicon as the hydride or halide and nitrogen as ammonia or an amine.

Considerably more exploratory research and pilot plant tests are necessary to determine if copper wire can be coated economically at a sufficiently rapid rate in a continuous process and yield properties competitive with polymeric-coated wire. A major commitment of money and a sharply-focused program are required before sufficient information will be at hand to determine the economic practicality of silicon nitride-coated copper wire.

SUGGESTIONS FOR FUTURE WORK

The Center for Surface and Coatings Research at Lehigh University is willing to continue work on silicon nitride as a protective coating for copper and its alloys. In view of the current economic climate and the emphasis on utility of research, it is essential that any future work be defined concisely and narrowly and that it be in accord with a high-priority need of the copper industry.

It is assumed that a high-priority need of the copper industry is for a protective coating useful on large and small parts for indoor and outdoor exposure. It is further assumed that the coating process can tolerate a considerable cost.

It is suggested that work on silicon nitride as a protective coating be continued and that emphasis be placed on determining a limited number of properties as a function of rate and method of coating formation. The two methods to be explored include reactive sputtering in a glow discharge and deposition from a gas mixture containing nitrogen and silicon compounds using an rf glow discharge. The following properties of coatings of a similar thickness in the range of 200-1000 Å. should be determined:

- (1) Crystallinity as determined by X-ray diffraction analysis.
- (2) Macroscopic and microscopic appearance.
- (3) Porosity as determined by corrosion potential relative to gold in ammonium chloride solution by the method of Morrissey.
- (4) Electrical resistance as determined by potential drop across film when contacted with mercury.
- (5) Corrosion resistance when exposed to mildly corrosive media.
- (6) Tarnish resistance when exposed to the atmosphere.
- (7) Oxidation resistance when heated to 200°C. in air.
- (8) Adherence upon thermal cycling.

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