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TECHNICAL REPORT NO. 2

PHOTOELECTROCHEMICAL DEPOSITIONS OF MICROSCOPIC
METAL FILM PATTERNS ON Si AND GaAs

by

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The fabrication of semiconductor microelectronics has become increasingly dependent on high resolution photolithographic techniques. These methods tend to be complex and time consuming, and often require high vacuum conditions. We describe here a study of the selective photoelectrochemical deposition of microscopic metal film patterns on single crystal p-Si and n and p-GaAs substrates. The photodeposition of films of Cu, Ni, Pd and Au on these semiconductors was investigated.

The deposition of metal and metal oxide images on semiconductor electrodes in a photoelectrochemical cell has been reported for TiO₂, ZnO, SrTiO₃ and GaP substrates (1,2). There has been one report of light assisted electrochemical deposition of metal contacts on Si solar cell substrates (3), but the contact patterns were produced by masking and not by selective photodeposition.

The basic mechanism responsible for the photoelectrochemical deposition process is the chemical reduction of metal ions from solution by photogenerated electrons in the conduction band produced at illuminated areas of the semiconductor surface. The reduction process can be written as:



where Mⁿ⁺ are metal ions of charge n in the electrolyte and e⁻_{surf} and M_{surf} are electrons and metal atoms on the surface. The rectifying nature of the semiconductor-electrolyte junctions acts to separate the photogenerated electron-hole pairs at the surface (4). In the case of a p-type semiconductor, an external reverse (cathodic) bias voltage is applied with

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respect to a counter electrode while for an n-type semiconductor a forward (anodic) bias is required to achieve the optimum band bending in the rectifying junction. When a thin initial film of metal is deposited, it is expected that a Schottky metal-semiconductor junction is formed which itself produces a rectifying barrier at the surface and isolates the semiconductor from the effects of the electrolyte redox potential (5,6). The redox electrolyte will then form an ohmic contact with the metal coated surface.

The properties of the substrates studied were as follows: p-Si, phosphorous doped, (100) face, 0.1-1 Ω -cm resistivity (Semiconductor Processing Corp.); p-GaAs, zinc doped, (100) face, 0.48 Ω -cm (Laser Diode Labs); n-GaAs, silicon doped, (100) face, 0.0008-0.0007 Ω -cm (Laser Diode Labs). The following standard plating solutions were used: 1:4 diluted copper/pyrophosphate (7), nickel sulfamate (Technic nickel S), gold/cyanide (Technic Orotemp 24) and palladium/cyanide (Technic palladium RT). A solution of CuClO_4 in acetonitrile prepared by electrolytic reduction of $\text{Cu}(\text{ClO}_4)_2$ was also used for Cu deposition. Just before use, the substrates were etched for 30 seconds in concentrated HF for Si and in 4% Br_2 in methanol for GaAs.

The metal film patterns were generated by projecting a reduced image of a USAF-1951 resolution target on the semiconductor wafer mounted in a Teflon flow cell with a quartz window. Contact was made to the back side of the semiconductor wafer with a layer of indium foil backed against a brass disc. In the case of p-GaAs, contact was made directly to the

brass disc. A Canon fl. 8 55 mm camera lens was used for imaging. A 100W tungsten-halogen lamp, filtered with a Schott KG-2 IR cutoff filter, was used for illumination, providing intensities at the semiconductor surface in the range of 80 to 20 mW/cm², depending on the absorption by the plating solution. A constant current source was used in the pattern deposition experiments to maintain a constant plating current and to supply a bias voltage with respect to a platinum counter electrode. The photo-plating currents were used in the range of 25-200 μ A with voltages ranging from -1 to -2V. An Amel 551 potentiostat was used for measurements of the current-voltage curves which were made with a saturated calomel (SCE) reference electrode and a platinum counter electrode.

The cyclic current-voltage curve for the photoelectrochemical deposition of Au on p-Si is given in Figure 1. This curve is similar to those obtained for the other metals on p-Si, which also display photocurrent to dark current ratios in excess of 4:1 for voltages more negative than -0.8V (SCE). The current-voltage curve for the photodeposition of Au and Cu on p-GaAs, displayed significantly lower photocurrent/dark current ratios than obtained with the deposition on p-Si. We were unable to photodeposit Pd or Ni on p-GaAs.

The redox potentials of the plating solutions used, in volts vs. SCE, are as follows: Ni (-0.42), Cu (-0.27), Pd (-0.43) and Au (-0.18). The band gap for p-Si in an aqueous electrolyte is in the range of 0.6 to +0.5 \pm 0.4V (SCE) depending on the pH (8) and a band gap of -1.3 to +0.2V (SCE) was reported by Bindra et al. (9) for n-GaAs. The metal redox potentials are therefore within the band gaps of both semiconductors.

The photodeposition process on both p-Si and p-GaAs was found to be sensitive to temperature and the best results were obtained when the plating solutions were heated to the temperatures recommended for plating on metal surfaces (7). This was particularly true for the deposition of Ni on p-Si and Au on p-GaAs where large improvements in resolution and the photocurrent/dark current ratio were obtained on heating.

Photographs of a photodeposited pattern of Au on p-GaAs are given in Figure 2 at two different magnifications. The best resolution obtained was about 10 μ for both Au on p-GaAs and Cu on p-Si. The resolution appears to be limited by the nucleation phenomenon involved in the deposition process. Under the higher magnification (Fig. 2b), thin deposits appear as a conglomerate of small dots which grow in size as the deposition process continues. The overpotential for plating on these microscopic metal clusters is apparently low enough to permit them to grow outside the illuminated regions thus causing a loss in resolution. A similar phenomenon was observed by Bindra et al. (9) in a study of the dark electrodeposition of metals on n-type semiconductors. In this latter study a "spotty" growth behavior was found to occur when the metals had work functions close to or lower than those of the semiconductor substrates and uniform deposits were obtained with metals having higher work functions. This phenomenon was explained by the effects of the Schottky barriers formed by the metal deposits (9). Using the same reasoning, the deposition of metals with sufficiently low work functions, such as Zn, Cd and Sn, on p-Si and p-GaAs should produce Schottky barriers less favorable

to further plating and thus yield more uniform and better resolved deposits. The resolution is also eventually limited by the attenuation of the light by the metal films when they become sufficiently thick, and further plating proceeds as a result of the dark current. Also, slight improvements in resolution could be obtained by employing a higher quality imaging lens designed for high resolution printing.

The photocurrent efficiency for Cu deposition on p-Si was determined by comparing the integrated plating current with the amount of Cu actually deposited as measured by dissolving the deposit in nitric acid and analyzing the resulting solution with atomic absorption spectroscopy. The yield was found to be within experimental error ($\pm 8\%$) of 100%. The thickness of simple rectangular deposits were estimated from their mass and area assuming the normal density of 8.96 g/cc for Cu. Reasonably good resolution was obtained for deposits as thick as 0.4 μ . The deposition rate was estimated to be about 450 $\overset{\circ}{\text{A}}/\text{min}$ with a deposition current of 75 $\mu\text{A}/\text{cm}^2$.

The photodeposition of Ni, Cu and Au films on n-GaAs was also achieved. Only negative images, where the metal film deposits everywhere except at illuminated areas, were produced for Cu and Au. In the case of Ni deposition on n-GaAs, both positive and negative images were obtained depending on the bias voltage applied. The voltage limits differentiating positive and negative imaging were found to be difficult to reproduce. The phenomenon of negative imaging can be explained by the positive photovoltage produced at an n-type semiconductor-electrolyte junction when the applied bias voltage is sufficient to induce metal plating in the dark but too small to

reverse the band bending. Positive metal film images can be produced on an n-type semiconductor when the applied bias voltage is negative enough to reverse the direction of the band bending but not negative enough to produce significant dark plating. When the bias voltage was zero or positive, the illumination produced selective photoetching of the surface and the resolution of the resulting etched images were better than 2 μ . Photoelectrochemical etching of diffraction gratings on n-GaAs has been reported by Belyakov et al. (10). We were unable to obtain any negative or positive photodeposition on n-Si. This is probably due to passivation on the n-Si surface by silicon oxides formed from the anodic oxidation of the surface by water and dissolved O₂.

In some photodeposition systems such as Au on p-GaAs using the Technic Orotemp 24 solution, and Cu on p-Si using a solution of CuClO₄ in acetonitrile, well resolved photodeposition was observed in the absence of any external electrical contacts or voltages. This "electroless" photodeposition, however, occurred at substantially slower rates than obtainable when an external current path and bias voltage were employed. This phenomenon can be explained by the presence of localized current paths through the electrolyte set up between adjacent light and dark areas of the semiconductor surface. This type of photodeposition is not to be confused with the thermally driven "laser enhanced photoplatin" developed at IBM (11) which employs light intensities over four orders of magnitude higher than those used here. This "electroless" photodeposition process will be discussed in more detail in a later publication.

One potential problem encountered in this study was the generally low adhesion and/or softness of the metal deposits. Annealing Cu deposits on p-Si at 900°C for 20 min under a 95% Ar, 5% H₂ atmosphere eliminated this problem; however, such high temperatures are not always feasible. It should also be possible to obtain film adhesion by using a more thorough etching procedure on the semiconductor surface before deposition. Film hardness can be improved by employing hardening additives which are commonly used for electroplating on metal surfaces (7).

There are many potential applications for high resolution photo-electrochemical metal film deposition. These would include formation of microscopic Schottky barriers, p-n junctions, ohmic contacts, and high density erasable archival data storage.

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REFERENCES

1. T. Inoue, A. Fujishima and K. Honda, Chem. Lett. (Chem. Soc. Japan), 1197 (1978); J. Electrochem. Soc., 127, 1582 (1980).
2. F. Mollers, J. J. Tolle and R. Meming, J. Electrochem. Soc., 121, 1160 (1974).
3. L. A. Grenon, Fall Meeting of the Electrochem. Soc., Hollywood, FL, October 1980, Recent News, Paper No. 713 RNP.
4. S. R. Morrison, Electrochemistry at Semiconductor and Oxidized Metal Electrodes, Plenum Press (1980).
5. S. Menezes, A. Heller and B. Miller, J. Electrochem. Soc., 127, 1268 (1980).
6. Y. Nakoto, T. Ohnishi, and H. Tsubomurs, Chem. Lett. 883 (1975).
7. F. A. Lowenheim edit., Modern Electroplating, John Wiley and Sons, Third Edition (1974).
8. S. R. Morrison, B. H. Loo, M. S. Madon and K. W. Frese, Jr., Final Report, DOE Contract AC-01-79ET-23109, July 8 (1980).
9. P. Bindra, H. Gerisher and D. M. Kolb, J. Electrochem. Soc., 124, 1012 (1977).
10. L. V. Belyakov, D. N. Goryachev and M. N. Mizerov and E. L. Portnoi, Sov. Phys. Tech. Phys., 19, 837 (1974).
11. Optical Spectra, December 31, 1979.

FIGURE CAPTIONS

Fig. 1. Cyclic current-voltage curves for the photoelectrochemical deposition of Au on p-Si with illumination (—), dark current spotted (....).

Fig. 2. Photomicrographs of a photodeposited Au film pattern on p-GaAs. a) low magnification, b) high magnification showing spotted nature of deposit.

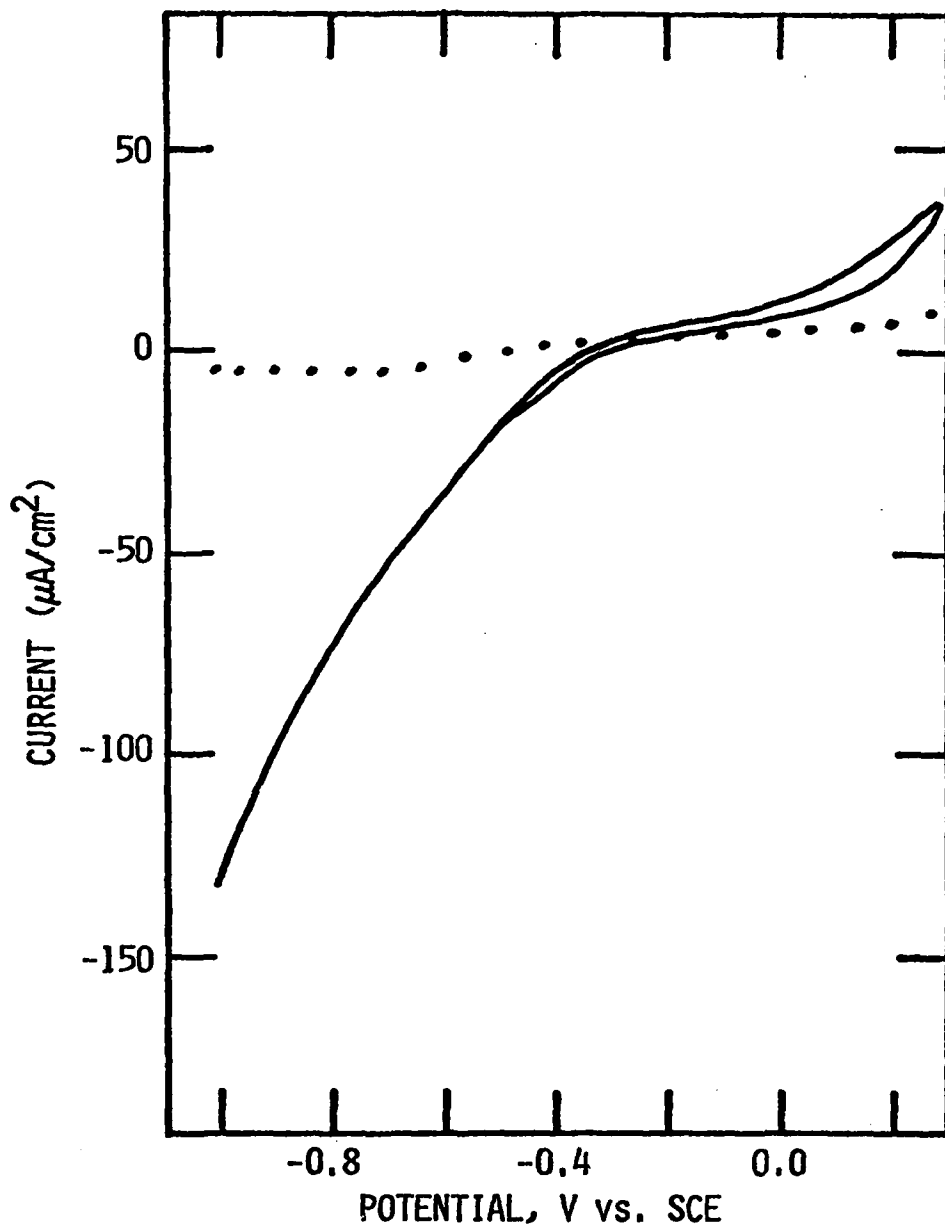
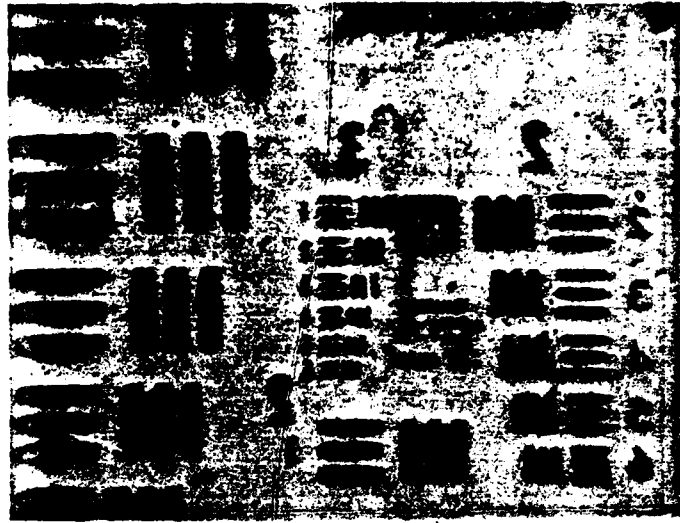
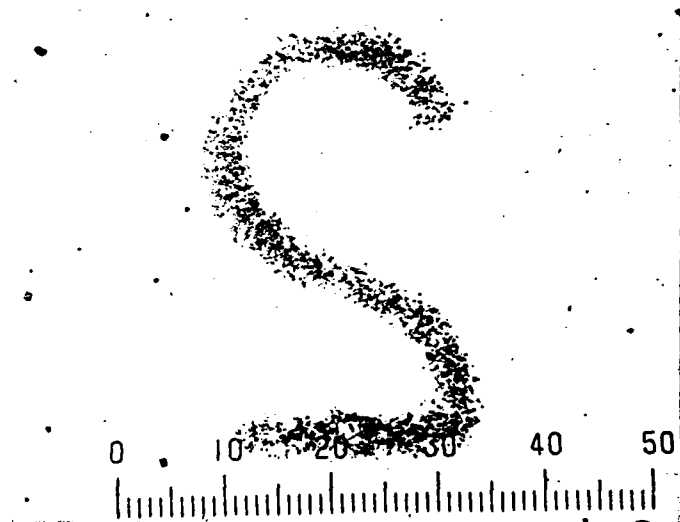


Figure 1



(a) 200μ



(b) 50μ

Figure 2

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