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FOR SEEDING OF ELECTROLESS Cu PLATING**

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Memorandum No. UCB/ERL M90/82

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ELECTRONIC SCIENCE LABORATORY

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# METAL VAPOR VACUUM ARC ION IMPLANTATION FOR SEEDING OF ELECTROLESS Cu PLATING

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## ABSTRACT

A Metal Vapor Vacuum Arc (MEVVA) ion source has been used to implant Pd into SiO<sub>2</sub> substrates. The ion implanted area formed a seeding layer on which a Cu film was successfully plated through an electroless plating process. It was found that the required Pd dose for Cu plating to occur is on the order of  $3 \times 10^{15}/\text{cm}^2$  when the implantation was performed with a 20 kV extraction voltage. Taking advantage of the large pulsed ion current capability (up to 1 Ampere) of the MEVVA ion source, the needed Pd dose for seeding was achieved in minutes. With direct Pd implantation, an intermediate activation step using PdCl<sub>2</sub> solution can be eliminated. The Cu plating rate was not a sensitive function of temperature and no incubation period was found in our experiments.

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## 1. INTRODUCTION

Simulation studies [1] on the circuit performance has shown that the delay time contributed by interconnection gradually takes over as the dominant factor when the device dimensions go down to the deep-submicron regime. The low electrical resistivity and expected high resistance to electron and stress migration have made copper a promising candidate for future interconnection material for its superiority over aluminum in operating speed and reliability. Therefore, copper has been investigated as a potential interconnect material for some time. Recently, the processing difficulty in patterning copper has been solved by employing the selective electroless plating technique [1]. Deposited and implanted Si, W and Ti have been used to initiate the copper nucleation process.

A high current metal ion implantation facility using a metal vapor vacuum arc (MEVVA) ion source [2-8] has been developed at Lawrence Berkeley Laboratory. With this apparatus, the relatively high Pd dose needed for the seeding process of electroless Cu plating can be achieved in minutes. Moreover, instead of depositing a seeding layer on the substrate, the "buried" seeds might even help the adhesion of the plated Cu film. In this report, we demonstrated that MEVVA can be applied to form Pd seeding patterns for selective electroless Cu plating on SiO<sub>2</sub> substrates, and direct Cu plating is feasible without a PdCl<sub>2</sub> activation step.

## 2. EXPERIMENTS

The MEVVA ion source is operated in a pulsed mode, with pulse width 0.25 ms and

repetition rate up to 100 pps. The beam current can be as high as several Amperes at peak and around 10 mA on a time average. Implantation was done in a broad-beam mode using the MEVVA ion source version V without magnetic charge-to-mass analysis of beam components, and the ion trajectories were line-of-sight from ion source to target.

In Figure 1 a schematic of the MEVVA ion implanter is shown. The vacuum pressure during implantation was typically in the low-to-mid  $10^{-6}$  Torr range. The target to be implanted was introduced into the vessel through an air lock, and was mounted on a water-cooled holder. A magnetically-suppressed Faraday cup can be inserted into the beam immediately in front of the target; the beam current can thus be adjusted prior to implantation and the number of beam pulses needed to accumulate the required dose can be calculated.

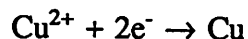
The ion beam charge state distribution was measured using a time-of-flight diagnostic technique [9]. The detector measured the electrical current in the different charge/mass ( $Q/A$ ) states and provided a good measurement of the ion composition of the extracted ion beam. An oscillogram of the time-of-flight charge state spectrum for a Pd ion beam is shown in Figure 2. The fractions of 23%, 67%, 9% and 1% of Pd ions in the beam were in 1+, 2+, 3+ and 4+ charge states, and hence, with implantation energies of 20 keV, 40 keV, 60 keV and 80 keV, respectively.

The implanted Pd profile was analyzed with Rutherford Backscattering Spectroscopy (RBS). Since the implantation was performed at a relatively low energy, the Pd profile was shallow. For a 20 kV extraction voltage, the profile peak was only 26nm below the  $\text{SiO}_2$  surface

with a relatively high surface Pd concentration. Therefore, the electroless Cu plating was then carried out directly, without a stripping process to expose the Pd peak concentration. The electroless Cu plating bath composition is as following:

CuSO <sub>4</sub> -5H <sub>2</sub> O	7.5 g/L
NaOH	23 g/L
CH <sub>2</sub> O (37%)	10 ml/L
EDTA	25 g/L
KCN (1 g NaOH, then 1 g KCN to 1 L water)	10 ml/L
Gafac (3%)	75 ml/L

The pH value of plating solution was 13. With formaldehyde as the reducing agent, the overall electroless plating process on the palladium surface can be resolved into two electrochemical half reactions [10]:



By directly using Pd as the seeding for electroless plating, we eliminated the need for PdCl<sub>2</sub> treatment conventionally employed to activate the substrate before plating. This not only simplifies the electroless plating to a one-step process, but it also eliminates the possibility of undesirable metal deposition on non-selected area in the substrate.

### 3. RESULTS AND DISCUSSION

It has been reported that the rate constant of the oxidation reaction is an exponential function of temperature [11]. To study the sensitivity of Cu deposition rate on temperature variation, we have conducted a series of electroless plating experiments at various temperatures. Pure Pd foils with 5 cm<sup>2</sup> surface area were plated in the bath at a temperature range from 30 °C to 70 °C for 100 seconds. The weights of the Pd samples were measured before and after plating. The difference represented the amount of plated copper. The results are given in Figure 3. On the semi-log plot, a roughly linear dependence is observed. However, the activation energy  $Q_a$  was calculated to be 0.096 eV, a rather small value to have a significant effect on the plating rate. At 60 °C, the amount of plated Cu was approximately 1600 µg in 100 seconds. This corresponds to a solid Cu deposition rate of 3.6nm/s. Figure 4 shows the deposition rate dependence versus plating time on pure Pd foils. The plating bath was kept at 60 °C. As shown in the figure, copper grew almost linearly with time, and no significant incubation period was observed.

Blanket Si wafer with 1 µm thermal oxide was used for the initial seeding test. Pd was implanted into SiO<sub>2</sub> substrates at various doses from 5×10<sup>14</sup>/cm<sup>2</sup> to 2×10<sup>16</sup>/cm<sup>2</sup> with the MEVVA implanter using a 20 kV beam extraction voltage. As shown in Figure 5, a threshold Pd dosage on the order of 3×10<sup>15</sup>/cm<sup>2</sup> was required for Cu plating to occur.

For multilevel interconnection technology, maintaining a planar structure would facilitate the metallization by eliminating processing steps such as planarization. Therefore, selective Cu



plating on trenches with Pd implanted seeds was tested. The experimental procedure is shown in Figure 6. A SiO<sub>2</sub> substrate film was formed on Si wafer with wet oxidation at 1000 °C for 2 hours. Photoresist was used as mask. Then, 0.45 μm deep trenches on SiO<sub>2</sub> film were fabricated with dry etching. Pd ion implantation was carried out at 20 kV. After photoresist stripping by acetone, Cu electroless plating was performed. Figure 7 shows a picture of Cu film grown in Pd implanted trenches. The Cu plated lines shown are 2 μm wide.

#### 4. CONCLUSION

We have demonstrated that selective Cu plating on SiO<sub>2</sub> substrate can be achieved with implanted Pd seeding using a high current MEVVA ion source. At 20 kV extraction voltage, the threshold Pd dose required for Cu plating is about  $3 \times 10^{15}/\text{cm}^2$ . With direct Pd implantation, an intermediate activation step using PdCl<sub>2</sub> solution can be eliminated. The Cu plating rate was not a sensitive function of temperature and no incubation period was found in our process.

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## FIGURE CAPTIONS

Fig.1 Schematic of the MEVVA ion implanter.

Fig.2 Charge state distribution for Pd ion beam. The peaks correspond to  $Q = 1+$ ,  $2+$  (maximum),  $3+$  and  $4+$ , right to left. The signal is the electrical current collected by a Faraday cup.

Fig.3 Cu deposition rate versus temperature. Pure Pd foils with  $5 \text{ cm}^2$  surface area were used. The "plated Cu" means the total amount of Cu deposited on the whole Pd foil in 100

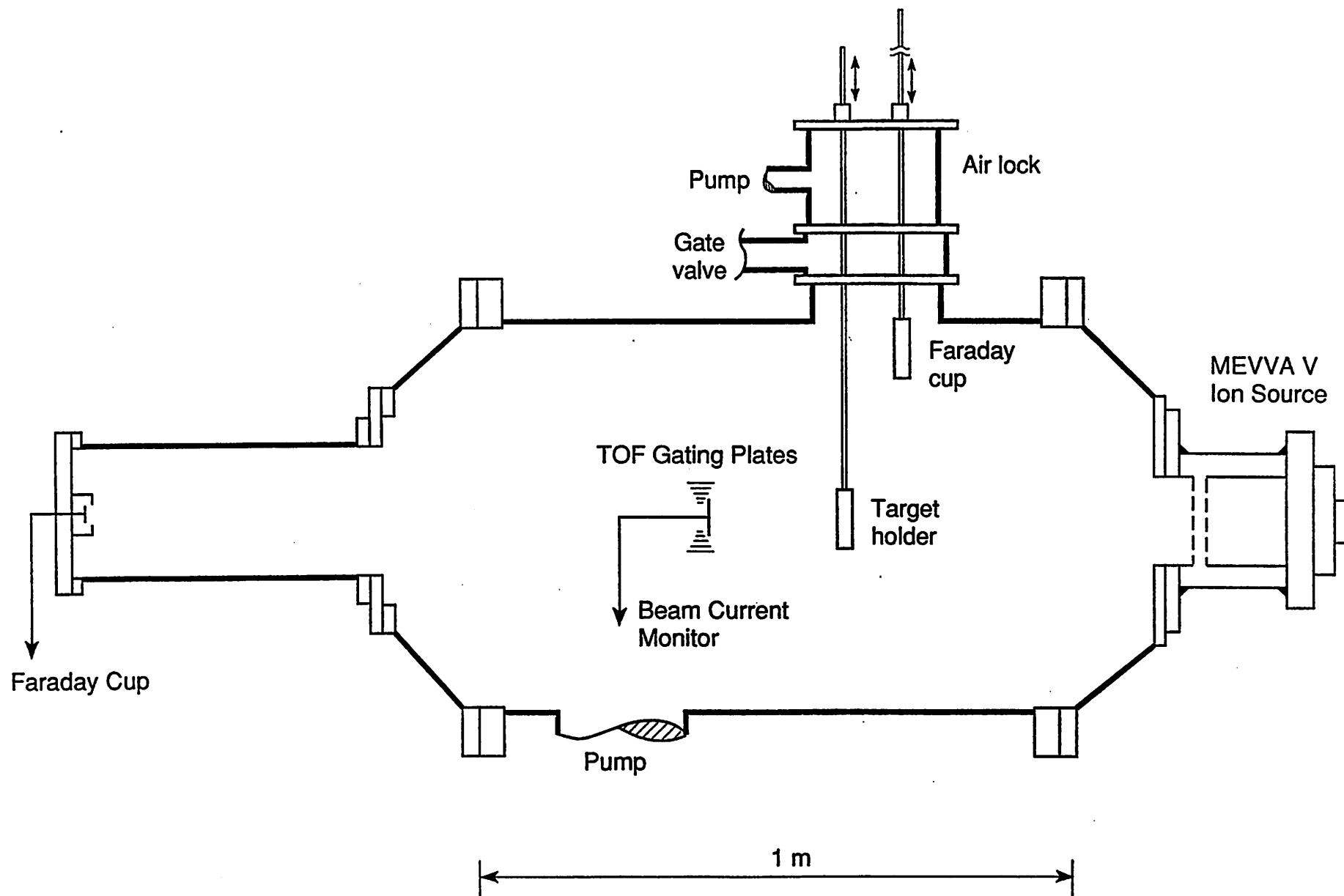
seconds. The calculated activation energy  $Q_a$  was 0.096 eV.

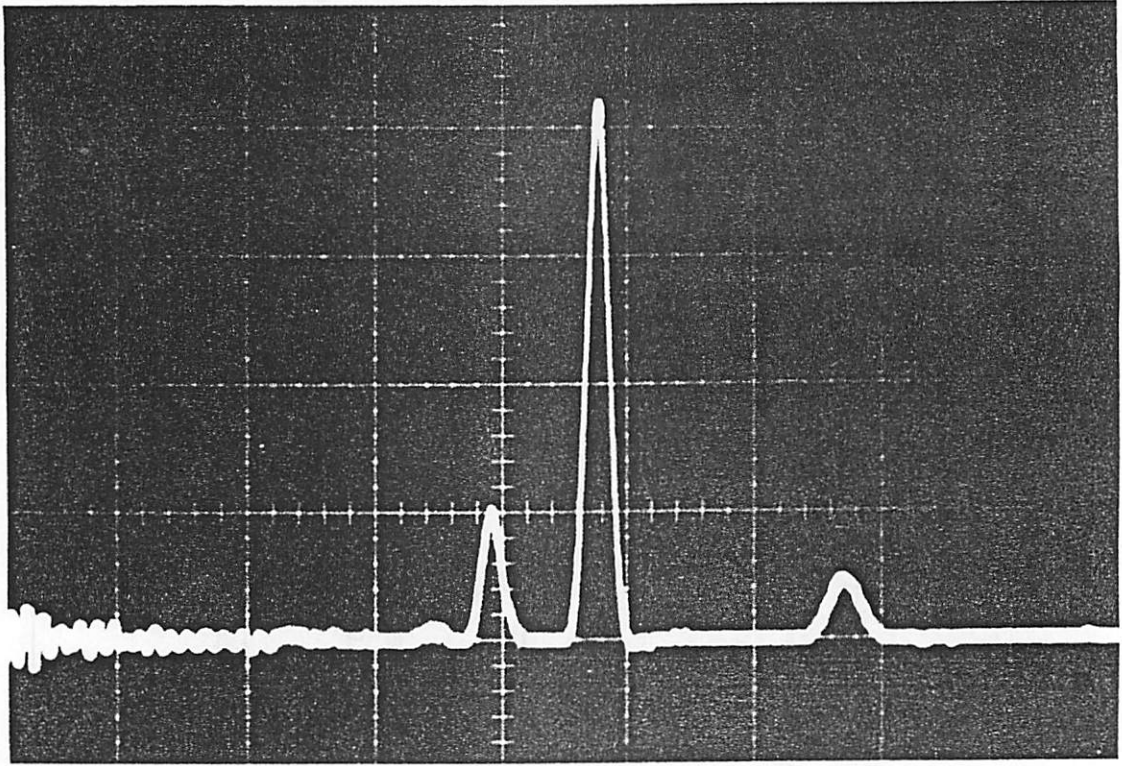
**Fig.4** Cu deposition rate versus time. Pure Pd foils with 5 cm<sup>2</sup> surface area were used. The "plated Cu" means the total amount of Cu deposited on the whole Pd foil in the indicate time period. The plating bath was kept at 60 °C.

**Fig.5** Cu plating behavior on Pd dose. Pd was implanted into SiO<sub>2</sub> substrate with the MEVVA implanter at a 20 kV beam extraction voltage. The threshold Pd dosage is on the order of 3×10<sup>15</sup>/cm<sup>2</sup>.

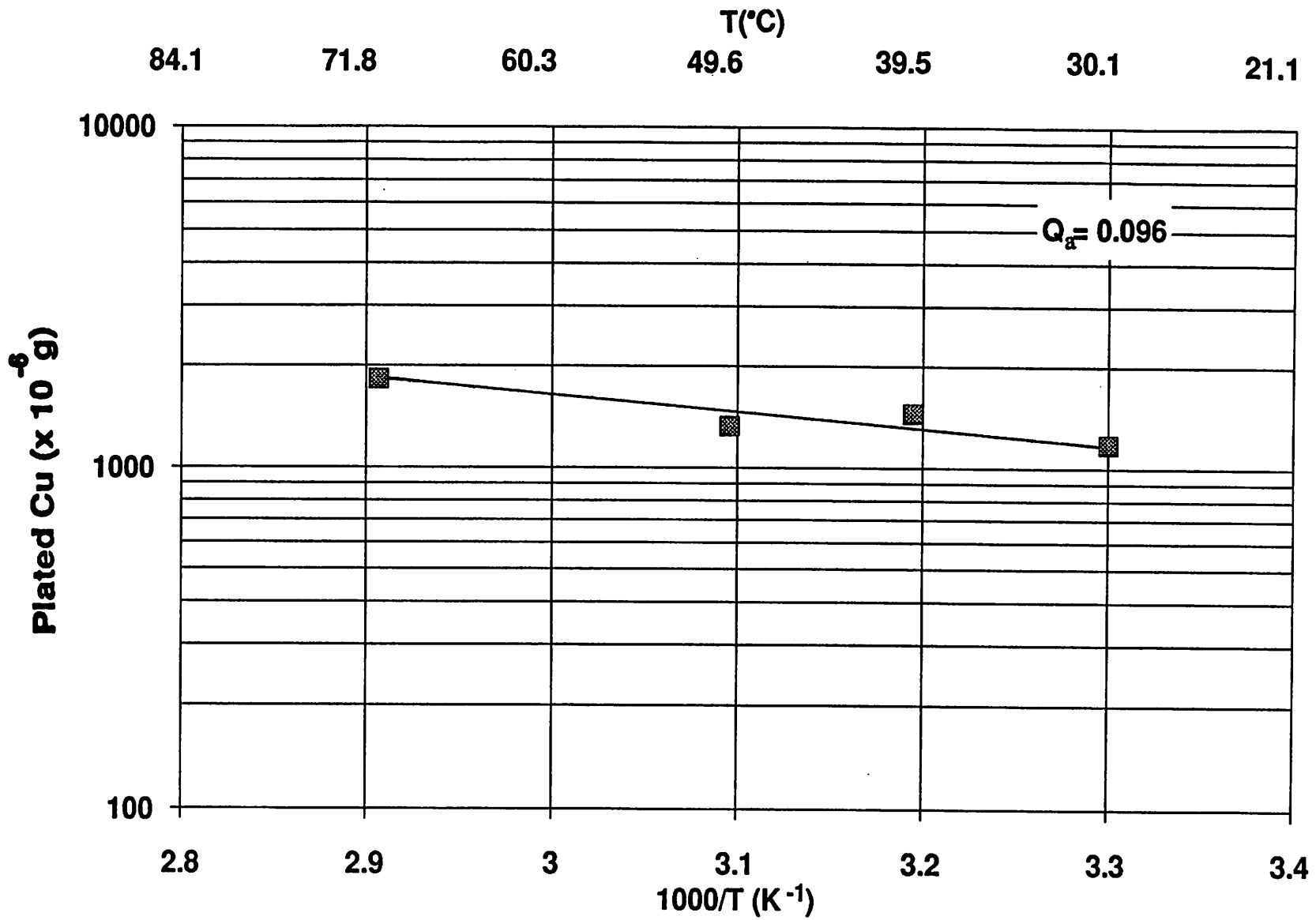
**Fig.6** The process flow of selective electroless copper plating: 1. Wet oxidation followed by photoresist pattern and reactive ion etching; 2. Pd ion implantation and photoresist removal; 3. Electroless Cu plating.

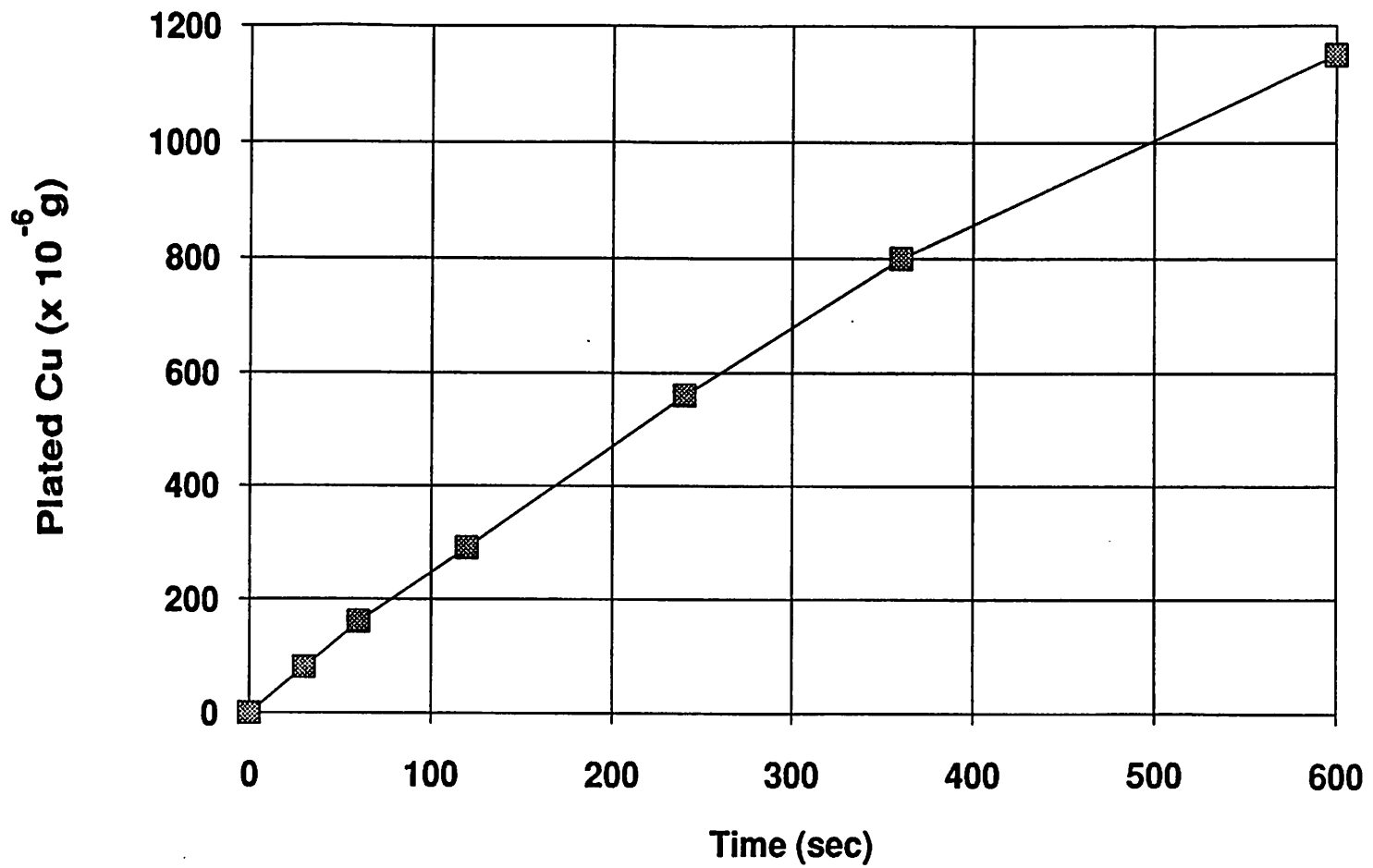
**Fig.7** Optical picture of selective electroless Cu plated on Pd implanted trenches. The Cu plated lines seen in the picture are 2 μm wide.

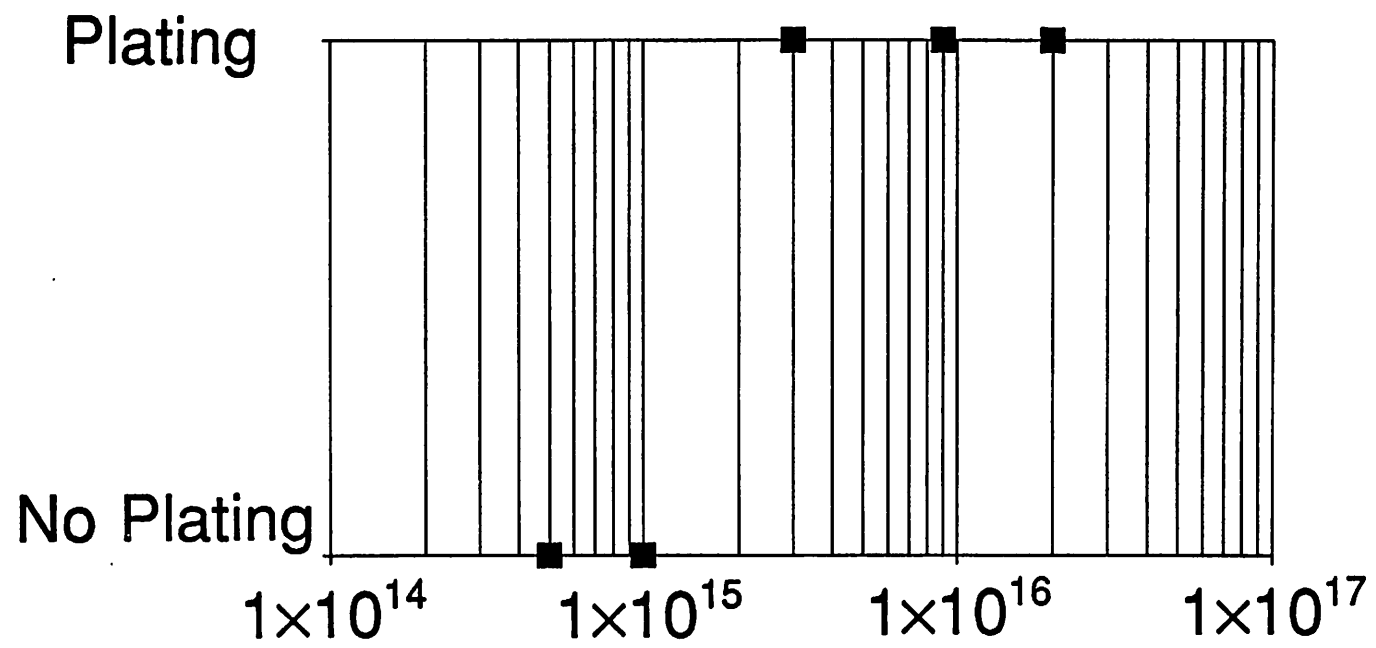




←  
P wave



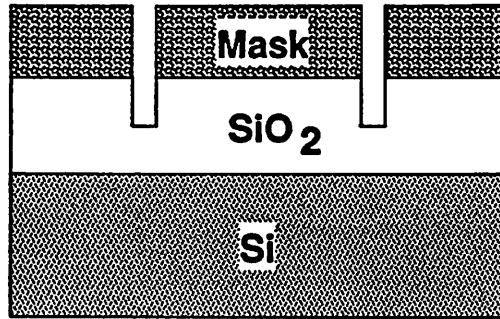




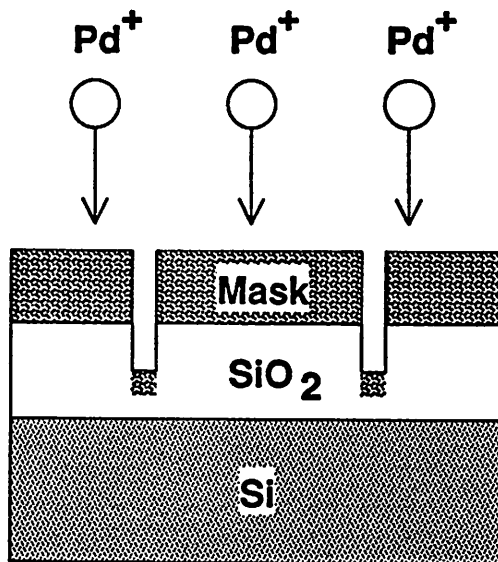
Pd Dose Measured by RBS



1.



2.



3.

