

AN ABSTRACT OF THE THESIS OF

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Title: VACUUM DEPOSITION OF SILICON MONOXIDE SEE-THROUGH  
MASKS *Redacted for Privacy*

Abstract approved: \_\_\_\_\_  
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The feasibility of evaporated silicon monoxide films on glass substrate to be used as masks in integrated circuit and device fabrication is examined. Experimental procedure for evaporating silicon monoxide is investigated. The effects such as source temperature and pressure on deposition rate are studied.

It is found that using conformal masking technique, silicon monoxide masks can be made; and pressure of  $\sim 10^{-6}$  mmHg, evaporation rate  $\sim 16 \text{ \AA}/\text{sec}$  and thickness of  $\sim 9650 \text{ \AA}$  to  $13,500 \text{ \AA}$  will yield silicon monoxide films that are semitransparent and yet block enough ultra-violet light to be useful as masks.

The transmission spectra of silicon monoxide films and films of  $\text{SiO}_x$  ( $1 < x \leq 2$ ) are measured.

The adherence of the silicon monoxide films to glass substrates is good provided the substrate is carefully cleaned.

The resolution of the silicon monoxide masks obtained is around 2.5 microns whereas the resolution obtained on silicon wafer by exposing through an SiO<sub>2</sub> mask is around 3 to 5 microns.

The optimum exposure time for the silicon monoxide films to block tungsten light is determined for different thicknesses.

Mechanical properties and susceptibility to scratching of the silicon monoxide film are investigated. Problem areas and limitations related to mask-making are discussed.

VACUUM DEPOSITION OF SILICON MONOXIDE

SEE-THROUGH MASKS

by

Kai-Yuan Wang

A THESIS

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Dean of Graduate School

Date thesis is presented April 1, 1971

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depends on conditions of evaporation which determine the optical properties of the films.

There are several methods by which such oxide films can be obtained, but each possesses its own inherent difficulties and generally require the use of a vacuum system as well as a high source temperature. Three methods of evaporating silicon monoxide are commonly used (4, p. 4): a) boat source; b) radiation-heated source; and c) embedded filament source. All these sources suffer from several undesirable characteristics which would result in poor quality films with many pinholes. To overcome this problem, several different evaporator sources have been designed with one basic design consideration: namely, elimination of a direct line of sight from the evaporant to the target (9, p. 1). These newly designed evaporators have made a great improvement over the exposed designs and are commercially available. A multi-baffled boat, which is one of the several newly designed silicon monoxide sources by the R. D. Mathis Company, was chosen to be used in this thesis project.

It has been shown by Hass that  $\text{SiO}_2$  films have strong ultra-violet absorption extending into the visible region (6, p. 184). The amount of absorption increases with film thickness. But the composition of the film depends on the deposition rate and residual pressure during evaporation (6, p. 185). Slow deposition rate and high residual

pressure would produce mostly  $\text{SiO}_2$  and an intermediate oxide,  $\text{SiO}_x$ ; where  $x$  varies between 1 and 2 (4, p. 8).

The purpose of this thesis is to study the feasibility of evaporated SiO see-through masks to be used in the fabrication of integrated circuits and devices.

The main requirement of a mask is for the masking material to block ultra-violet light. This is met by the strong absorption properties of the SiO film in the ultra-violet region. The semi-transparency of the SiO mask in the visible range is an added advantage over conventional masks and facilitates aligning masks together.

An investigation of the effects of evaporation variables like residual pressure and deposition rate on the transmission spectrum of the film should aid in understanding the interrelationship between preparation condition and optical properties of the films.

The thesis is divided mainly into two parts. The first part deals with the preparation of the substrate and the evaporation of the SiO material. The second part is concerned with evaluation of the evaporated films and with the condition of evaporation on deposition rate and composition of the films. The etching properties and the resolution obtained on films are studied. Thickness, exposure test and transmission spectra are measured on

films of different thicknesses. The effects of source temperature on deposition rate and the effects of pressure during evaporation on the composition of film were studied. The mechanical properties of the film and resolution obtained on the silicon wafer were also investigated.

A flow chart shown in Figure 1 outlines the general procedure followed in this project.

Two techniques were used for making patterns on the SiO films. In the first technique, Etching Process was used; the substrates were deposited with SiO films first, then patterns were etched on the film. The second technique used a Lift-off Process. In this technique, photoresist on the substrates was exposed with uv light through a pattern plate and developed. Then SiO film was deposited on top, the photoresist was stripped away, which also removed the overlying SiO film but left the SiO film on the substrates in areas without photoresist.

After Preparation of Substrates, seven substrates were grouped as follows: two substrates were separated for Etching Process to make patterns on SiO film; two were processed for the Lift-off technique to make patterns; one substrate each designated for Thickness Measurement, Exposure Test and Measurement of Transmission spectrum respectively. These last three substrates were the ones not used for pattern generation.

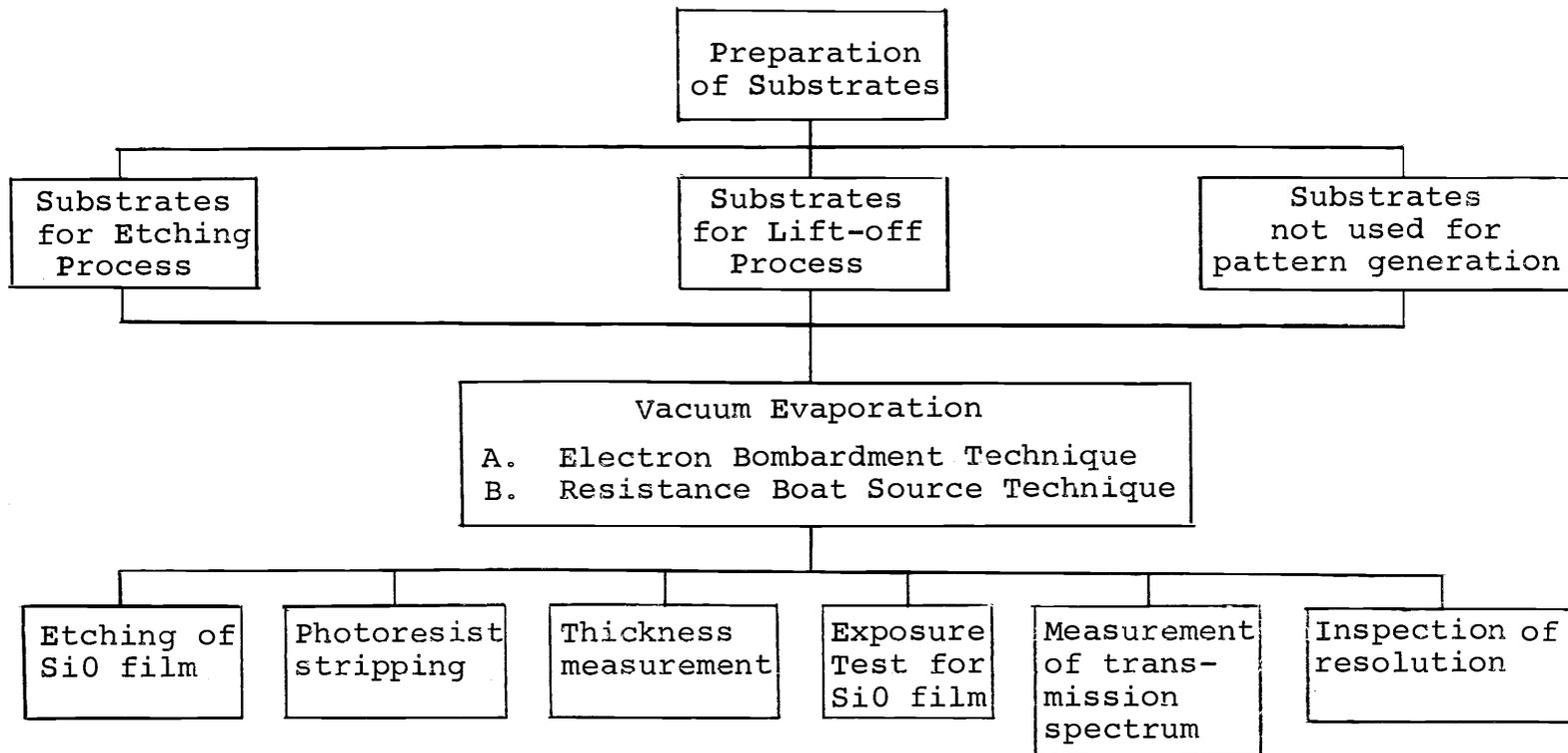


Figure 1. Flow chart diagram showing general procedure.

## II. PREPARATION OF SUBSTRATES

Substrate cleaning is essential for good adherence of film material. Microscope cover glasses of 0.6" x 0.6" were used as substrates.

First, the substrates were cleaned by the following procedure to remove dirt, oil and organic materials (4, p. 7):

- A. Washing in detergent for two minutes followed by rinsing in DI (deionized) water.
- B. Boiling in mixture of sulfuric acid and chromic acid for five minutes at 100°C, followed again by rinsing in DI water.
- C. Ultrasonic cleaning in acetone for five minutes, followed by rinsing in DI water.
- D. Ultrasonic cleaning in hydrogen peroxide for five minutes.
- E. Rinsing in DI water for five minutes.

The substrates were then blown dry by nitrogen, baked on a 150°C hot plate to dry completely, and stored between layers of clean filter paper and kept in a dust-free compartment ready for further processing.

Two techniques were used for mask pattern generation.

In the first technique Etching Process was used. The film was evaporated on the substrates, then photoresist was applied and a resolution pattern exposed with

ultra-violet light. The substrates were developed and etched in an SiO<sub>2</sub> etchant to register the pattern. The substrates to be used in this technique need no more processing after being cleaned.

The second technique used a Lift-off process to make conformal masks (1, p. 452). In this technique photoresist was applied to the cleaned substrates after drying them in 400°C annealing furnace. Several photoresist coatings were applied to the substrates. Then the substrates were exposed to tungsten light for four seconds through a resolution plate (with pattern of lines and spacings of different magnitude), which will be described further in a later section. After developing the photoresist AZ 1350 the substrates were rinsed in DI water and blown dry with nitrogen. At this point windows were opened in places where the photoresist had been exposed. After evaporating SiO<sub>2</sub> on the substrates they were immersed in a photoresist stripping solution, which removed the overlying layer of SiO<sub>2</sub> film but left the SiO<sub>2</sub> film in the window areas intact. This procedure provided a sharp edge definition and there was no attack on the substrates.

The substrates to be used in this second Lift-off technique had resolution pattern of photoresist already developed prior to vacuum evaporation of the SiO<sub>2</sub> film.

The substrates not used for pattern generation required no additional processing after being cleaned.

Vacuum evaporation and the Photoresist Stripping for the Lift-off Process are detailed in Sections III and IV.

### III. VACUUM EVAPORATION OF THE SILICON MONOXIDE FILMS

Two techniques were used to evaporate silicon monoxide films. The first technique was by means of electron bombardment using an electron gun (e-gun). The second technique was by using a resistance boat source.

#### A. Experimental Setup

The equipment used for the deposition of SiO film is a Varian Vacuum System. The main components of the system are bell jar, base plate, mechanical roughing pump, VacIon pump, titanium sublimation pump, valves, substrate holder, deposition thickness monitor, e-gun, silicon monoxide evaporation boat, Varian filament power supply, control units and the hardware installed in the bell jar.

The vacuum chamber consists of a standard 18-inch diameter by 30-inch high Pyrex bell jar and a steel staging platform.

The roughing system is used to reduce pressure in the vacuum system from atmosphere to below ten millitorr (one millitorr = one micron Hg). A 17.7 cfm Edwards mechanical pump is used. A molecular sieve trap, located between the pump and the chamber, minimizes back-streaming of oil and aids in pumping water vapor.

The VacIon pump provides completely clean, vibration-free pumping. It removes gases by gettering chemically

active gases, ion burial of heavy noble gases, cracking and gettering of complex molecules, and by diffusion of hydrogen and helium into the titanium cathode plates. It can be completely isolated before the chamber is opened to air.

One of the silicon monoxide evaporation sources consisted of a resistance-heated baffled boat, as shown in Figure 2. A cross section view is shown in Figure 3. The boat is designed to meet the necessary requirements of evaporation rate, input power and prevention of particles of the bulk material from leaving the source before changing into gas phase. The SiO source made from tantalum was filled with 6.5 grams of SiO powder (SiO material originally in lumps was ground to approximately 120 grit powder). The ends of the boat were clamped to two electrodes which were connected to a Varian filament power supply that furnished approximately 200 amperes at five volts ac. This heated the boat to approximately 1000°C.

The Sloan Instrument deposition thickness monitor, model DTM 3, was used for monitoring and control of thickness of the deposited silicon monoxide films. The mass of the deposit was measured by evaluating the frequency change of an oscillating quartz crystal inside the vacuum system as deposit built up on its surface. The thickness monitor was set up at the same distance from the source as the

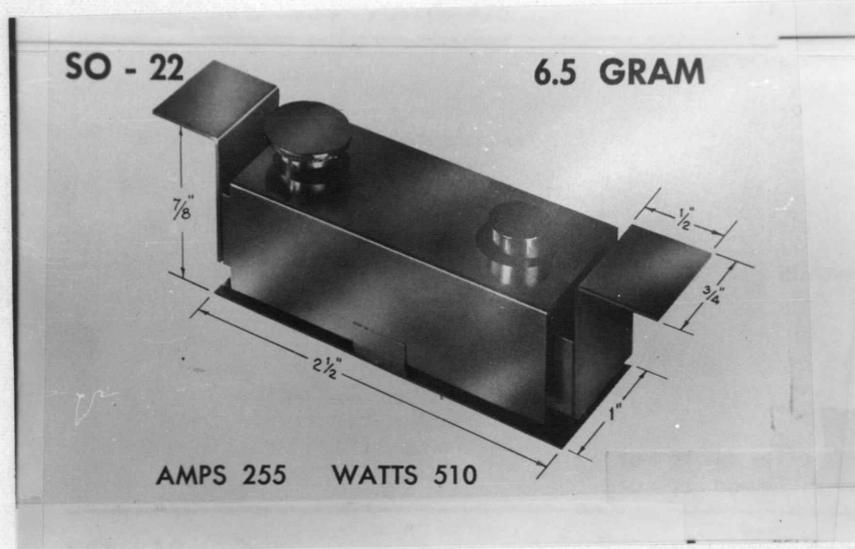


Figure 2. Baffled boat source for evaporation of  $\text{SiO}_2$ .

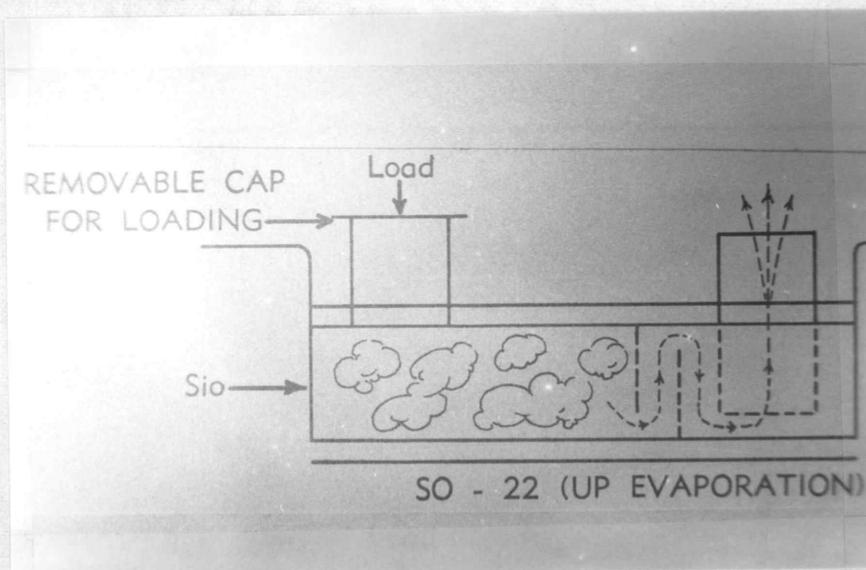


Figure 3. Cross section of the baffled boat source.

substrate on the substrate holder.

The other evaporation source was an electron bombardment type (Varian e-gun). It consisted of a filament (source of electrons), focussing magnet, and a water-cooled three crucible block (target). The focussed electron beam from the filament strikes the evaporant material placed in the center of the water cooled crucible. The 2000-watt maximum power of the beam is sufficient to evaporate refractory and dielectric materials as well as more common conductive and semiconductor materials.

The e-gun source unit provides convenient single knob control of evaporation. It is also connected to a water-flow interlock and pressure interlock.

## B. Experimental Procedure

(1) Electron Bombardment Technique. In a typical electron bombardment procedure, the prepared substrate was mounted on the substrate holder. The substrate and its holder was then placed in the vacuum system. A chunk of SiO was then placed in the e-gun crucible in the vacuum system. The shutter was closed over the evaporation port. The bell jar was lowered and the mechanical roughing pumping was applied by opening the appropriate valve. When the chamber pressure decreased to 15 millitorr,

the titanium sublimation pump was turned on, and when the pressure decreased to ten millitorr, the mechanical pump was disconnected by closing the appropriate valve. The isolation valve of the VacIon pump was slowly opened. Both the titanium sublimation pump and the VacIon pump continued to evacuate the system until the chamber pressure decreased to  $10^{-7}$  torr (it took several hours).

Next, the deposition monitor and the substrate heater were turned on. After a few minutes, the substrate temperature reached  $70^{\circ}\text{C}$ . Then the water valve to the e-gun water-cooling system was turned on and the beam current was increased to ten milliamperes. After 15 minutes, the evaporation source (SiO) was heated up. Then the beam current was slowly increased until the SiO began to evaporate (the average beam current was about 50 milliamperes). The frequency of the deposition monitor was set in an appropriate position corresponding to the desired film thickness and the shutter was opened at the same time when a stop watch was clocked.

The SiO was deposited on the substrate and the deposition monitor exhibited the frequency shift. When the SiO reached the required thickness, the power supply turned off. Then the shutter was closed, the stop watch stopped and the deposition monitor, the substrate heater, and the titanium sublimation pump were turned off. The pressure in the vacuum system during the e-gun deposition was

maintained in the  $10^{-6}$  mmHg range.

(2) Resistance Boat Source Technique. In a typical resistance boat deposition experiment, the same pumpdown procedure was followed. When the pressure was down to the  $10^{-7}$  mmHg range the supplies to the source and to the substrate heater were turned on and the boat heated to  $500^{\circ}\text{C}$  to outgas for 30 minutes and the substrate temperature reached  $70^{\circ}\text{C}$  while keeping the pressure in the appropriate range (normal range is in the  $10^{-6}$  mmHg for evaporation of true SiO). Then the voltage on the filament power supply was increased until the current read between 200 to 210 amperes, and the SiO source began to evaporate ( $\sim 1000^{\circ}\text{C}$ ). One minute was allowed for the SiO source to warm up and stabilize at the evaporation temperature. Meanwhile the thickness monitor was set to zero and the appropriate frequency range. The shutter was now opened at the same time when a stop watch was clocked.

The SiO film deposited on the substrate and on the deposition monitor crystal produced a frequency shift. When the SiO film reached the required thickness which corresponded to a certain frequency shift the shutter was closed, the stop watch stopped and the source supply turned off.

The titanium pump was shut off and the system allowed to cool for more than one hour before removing the substrate. After the cooling period nitrogen was connected

to the system to bring it to atmospheric pressure. The nitrogen was disconnected and the bell jar raised. The substrate was removed for further processing.

It was found that the boat evaporation method was much more convenient to use; there was no problem as in the e-gun method in positioning the electron beam, and one loading of SiO can easily be used in several evaporations; the source temperature can also be measured by a thermocouple welded to the walls of the boat. Consequently the boat evaporation method was used for subsequent evaporation.

In each evaporation run seven substrates were used. Four of these substrates were intended for pattern generation: two for the Etching Process; two for the Lift-off Process. The other substrates were intended for Thickness Measurement, Measurement of Transmission Spectrum and Exposure Test respectively.

Since the substrates were evaporated simultaneously and the distances between each substrate and the source were approximately the same, the thickness measured in the Thickness Measurement represented the thickness of the films on all seven substrates.

#### IV. POST-EVAPORATION TREATMENT OF SUBSTRATES

##### A. Photoresist Stripping for the Lift-off Process

The substrates undergoing the Lift-off process and with a resolution pattern on them were stripped of the photoresist which was applied prior to evaporation. This will remove the overlying SiO film as described in Section II.

A cross sectional view of the substrate shown in Figure 4 illustrates the technique of conformal masking.

The substrates were treated with the following stripping procedure:

1. Etch in buffered HF 4:1 for 15 seconds. This is to expose the photoresist underneath the SiO where the thickness of the SiO film is minimum by etching SiO. These are the regions over the edge of the windows of photoresist on the substrate.  
See Figure 3.
2. Rinse in DI water.
3. Ultrasonic cleaning in acetone for ten minutes.  
Acetone dissolves photoresist AZ 1350. This step loosens the photoresist layer if not removing it.
4. Rub the substrates immersed in acetone with a cotton swab. This removes the overlying SiO film on the photoresist.

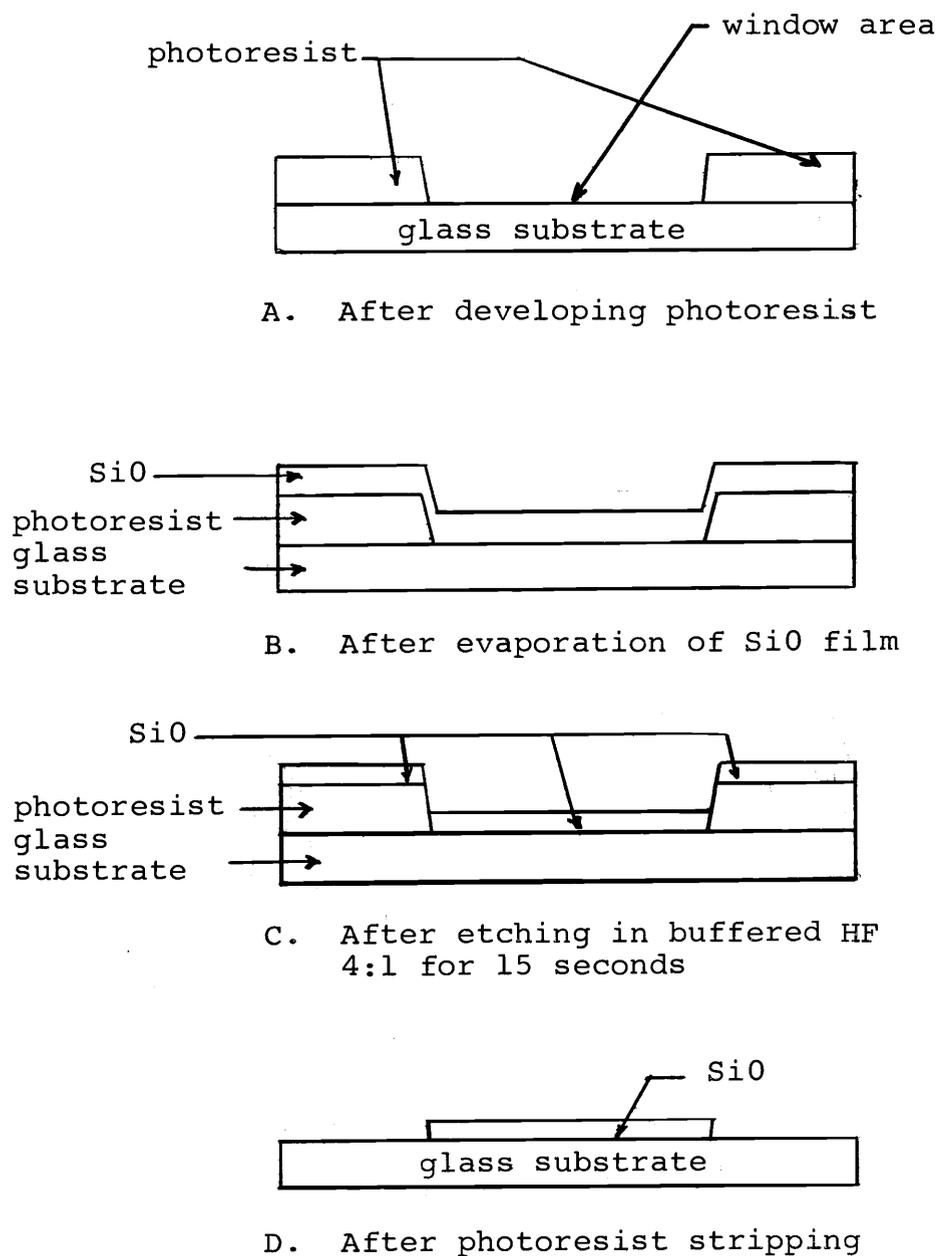


Figure 4. Technique of the Lift-off process to make conformal masks.

5. Rinse in DI water.
6. Dry with nitrogen.

#### B. Removal of SiO Films for the Etching Process

After photoresist was applied, exposed with a resolution plate and developed, the substrates were etched in an SiO etchant. The etchant was a mixture of buffered HF 4:1 and dilute nitric acid heated to approximately 100°C.

Unheated solution etched too slowly to be useful. Since the etchant also attacked the glass substrates it was very hard to control the rate and the time of the etch. Overetching produced streaks and opaqueness in the glass.

This method was rather unsatisfactory, thus was abandoned in favor of the Lift-off process.

#### C. Inspection of Resolution

The substrates undergoing the Lift-off process were inspected under the microscope for the resolution obtained.

The resolution of a photographic pattern is often given in terms of cycles per millimeter, where a cycle consists of a line and an adjacent space.

For our purpose we are interested in the resolution of the mask, in millimeters per line or space.

Two resolution patterns (USAF 1951) on high resolution emulsion plates were used in making SiO masks: one dark

field and one light field (one the negative of the other).

Figure 5 and Figure 6 show the resolution obtained on the SiO masks from the dark field resolution plate and the light field one respectively. A scale is also shown in each photograph. Each division of the scale is 0.01 mm (10 microns) or  $\sim 0.4$  mils. The first element of Group 1 in Figure 5 shows that lines or spaces of a width of  $\sim 2.5$  microns can be distinguished. In Figure 6, lines or spaces of a width less than 5 microns can be distinguished as shown by the 6th element of Group 0.

#### D. Adherence Test and Inspection for Pinholes

An important characteristic of the film is its adherence to the glass substrate. The Scotch tape test was used to examine the adherence of the SiO films. A strip of Scotch tape was applied to the film, rubbed in place, and then stripped off. The film passed the test.

The SiO films were inspected for pinholes, using a high power microscope. There were very few pinholes observable. On five samples there were less than four per  $\text{mm}^2$ .

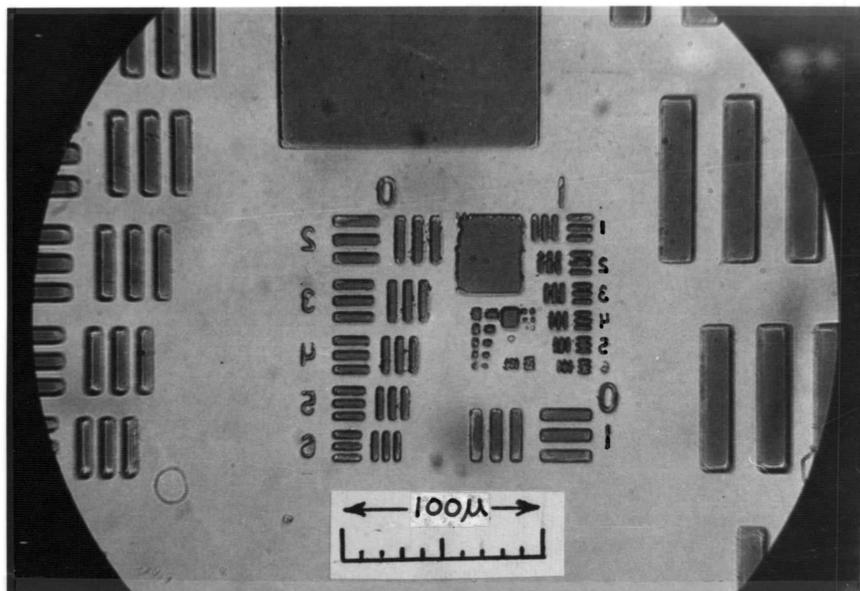


Figure 5. Resolution obtained on SiO<sub>2</sub> film from the dark field resolution plate. (Dark area is SiO<sub>2</sub>; clear section is glass substrate)

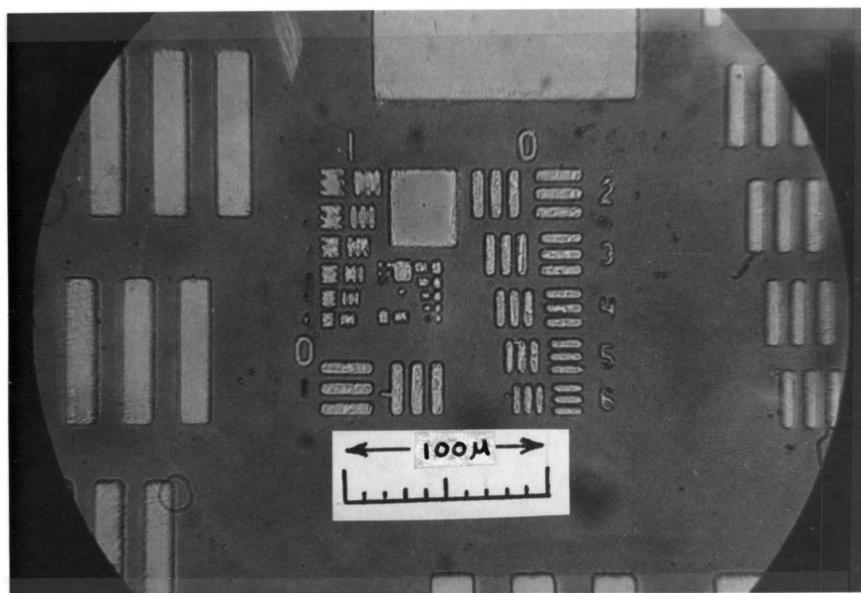


Figure 6. Resolution obtained on SiO<sub>2</sub> film from the light field resolution plate. (Dark portion is SiO<sub>2</sub>; clear area is glass substrate)

## V. THICKNESS MEASUREMENT OF SiO FILMS

### A. Multiple-beam Interference Method

The substrate was masked with a piece of copper wire 1.5 mm in diameter during evaporation of SiO to give a graded step of SiO film on the surface. It was then metallized with a film of Al on the whole surface with a vacuum evaporator. One surface of a glass piece was silvered to approximately 80% reflecting. The silvered surface of the glass piece was placed in contact with the metallized surface of the substrate across the graded step. The combination was examined with a Unitron metallurgical microscope equipped with a monochromatic sodium light source ( $\lambda=5893 \text{ \AA}$ ). Light entering the combination underwent a series of multiple reflections giving rise to alternate light and dark fringes. The displacement of the fringes across the step is related to the film thickness by the following equation (2, p. 1206):

$$d = p \frac{\lambda}{2}$$

where  $d$  = the film thickness

$p$  = the number of fringe displacement

$\lambda$  = the wavelength of the monochromatic light

The accuracy of the measurement was estimated to be 0.02 fringe corresponding to  $\pm 59 \text{ \AA}$ .

### B. Vacuum Deposition Thickness Monitor

The deposition thickness monitor was calibrated for SiO films and the particular vacuum system. It was calibrated by evaporating various thicknesses of films onto the substrates and recording the corresponding change in frequency.

Under evaporation condition the pressure was maintained at approximately  $4 \times 10^{-6}$  mmHg; the source current was  $\sim 200$  amperes; the distance between the source and the substrate was 5.1 inches.

The actual thicknesses of the films were measured by using the multiple-beam interference method as described in the previous section. The mean values of SiO thickness versus deposition monitor frequency change are shown in Figure 7. The mean thickness is the arithmetic mean of five samples. The 95% confidence interval was calculated using a student's t distribution. It is evident that the deposited thickness is directly proportional to the frequency change.

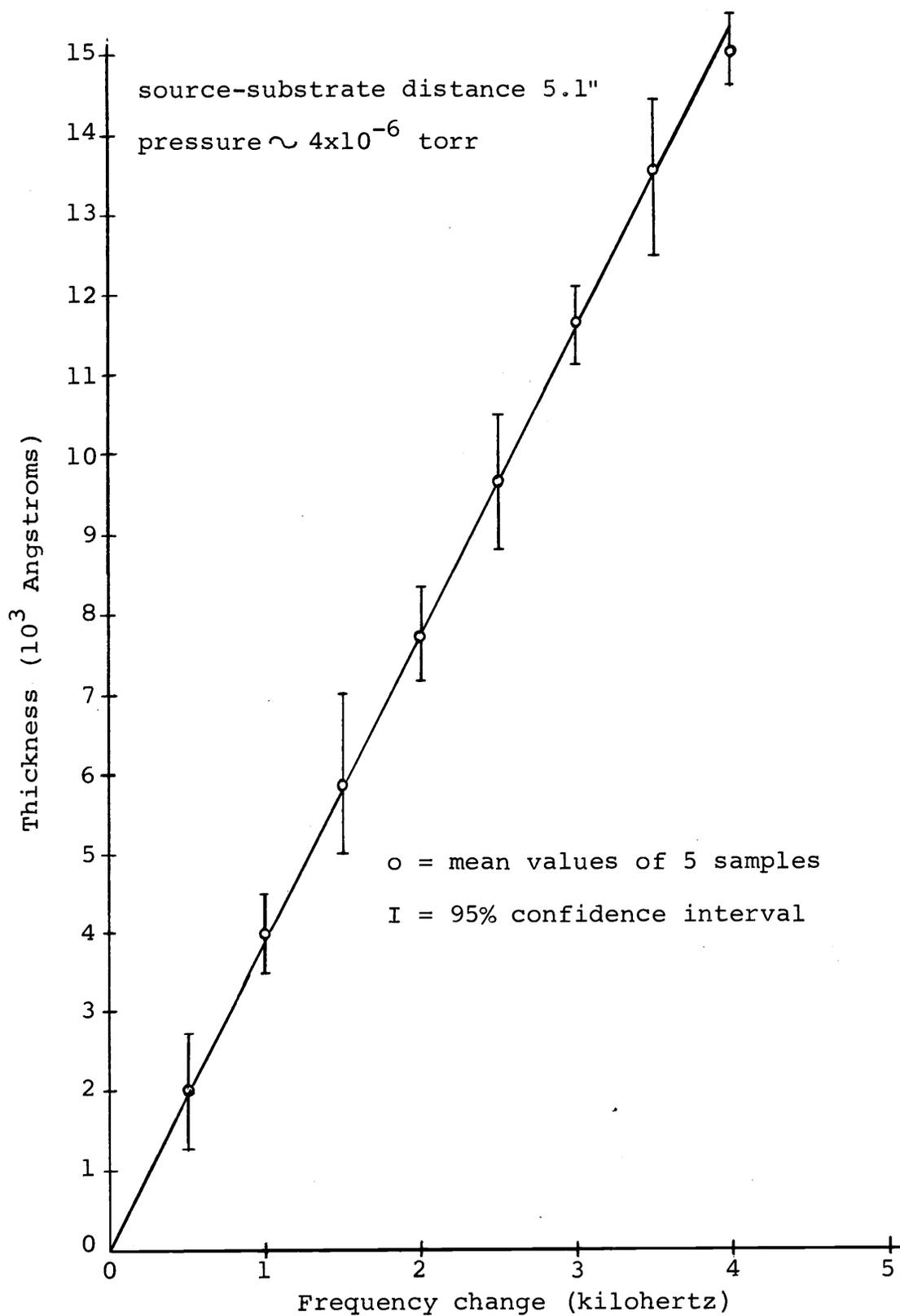


Figure 7. Calibration curve of film thickness versus monitor frequency change.

## VI. DEPOSITION CONDITION OF SiO FILMS

### A. Effect of Source Temperature on Deposition Rate

The thickness variation as a function of deposition time for different source temperatures is shown in Figure 8 (Table I). These curves are plotted for source temperatures of 1075°, 1150° and 1250°C. It is noted that the thickness of SiO film varies linearly with deposition time.

Figure 9 (Table II) shows the deposition rate versus source temperature for a source-to-substrate distance of 5.1 inches with vacuum pressure of  $\sim 4 \times 10^{-6}$  torr. The curve indicates that the deposition rate increases linearly with source temperature from about 1200° to 1300°C. The experimental results agree fairly well with the findings of a number of investigators (8, p. 319) that deposition rate depends to a large extent on source temperatures.

### B. Effects of Deposition Rate and Pressure of Evaporation on Composition of SiO Film

It has been found that the composition of the evaporated film is dependent on the deposition rate and the pressure of evaporation (5, p. 353). At pressures of  $\leq 1 \times 10^{-5}$  mmHg and deposition rates of  $> 10 \text{ \AA}^{\circ}/\text{sec}$ , true films of SiO have been obtained with very little SiO<sub>2</sub> (6, p. 181). The evaporated SiO is amorphous and the characteristic dark brown color is the

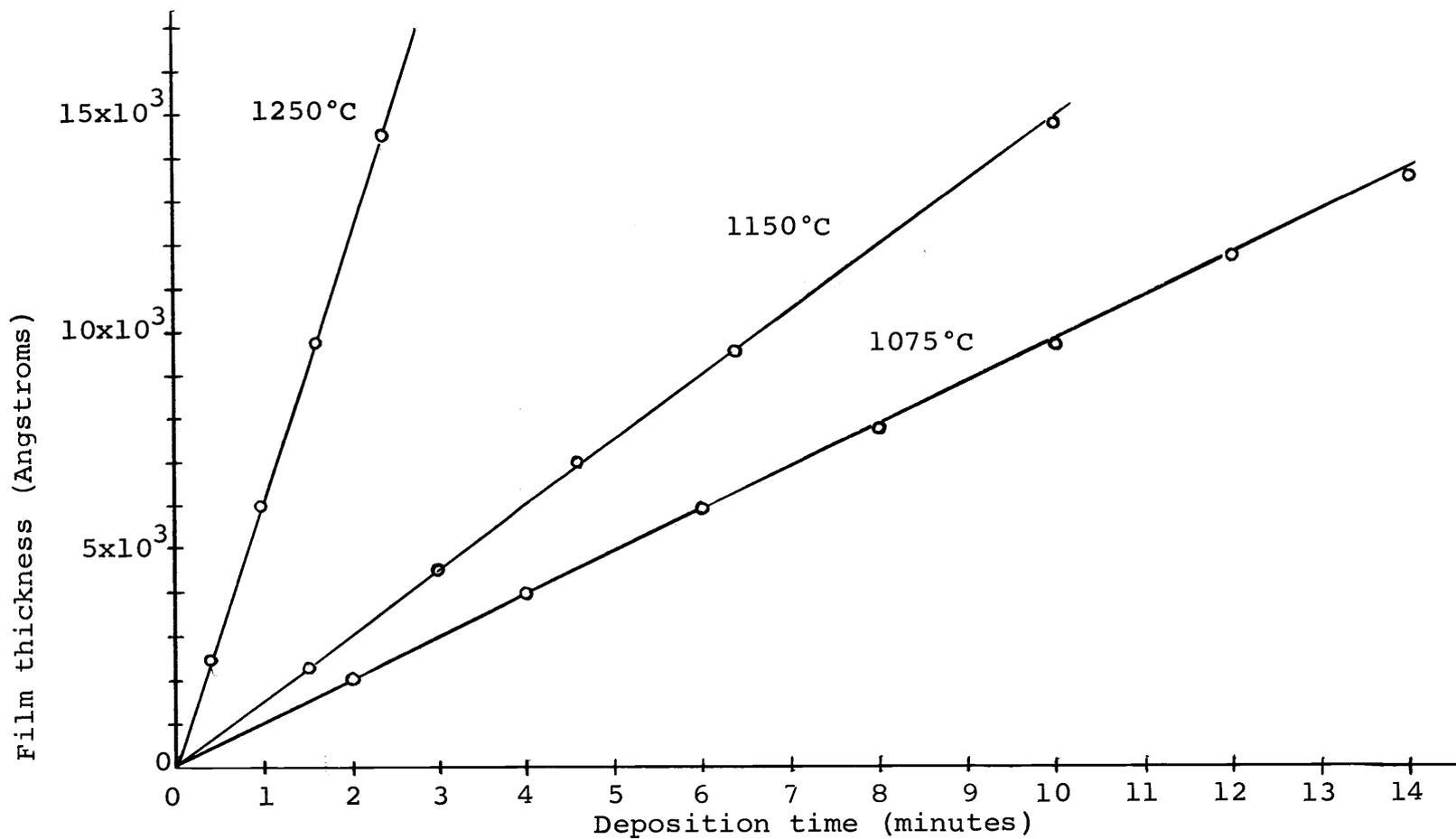


Figure 8. Film thickness versus deposition time for various source temperatures at a source-substrate distance of 5.1 inches and bell jar pressure of  $4 \times 10^{-6}$  torr.

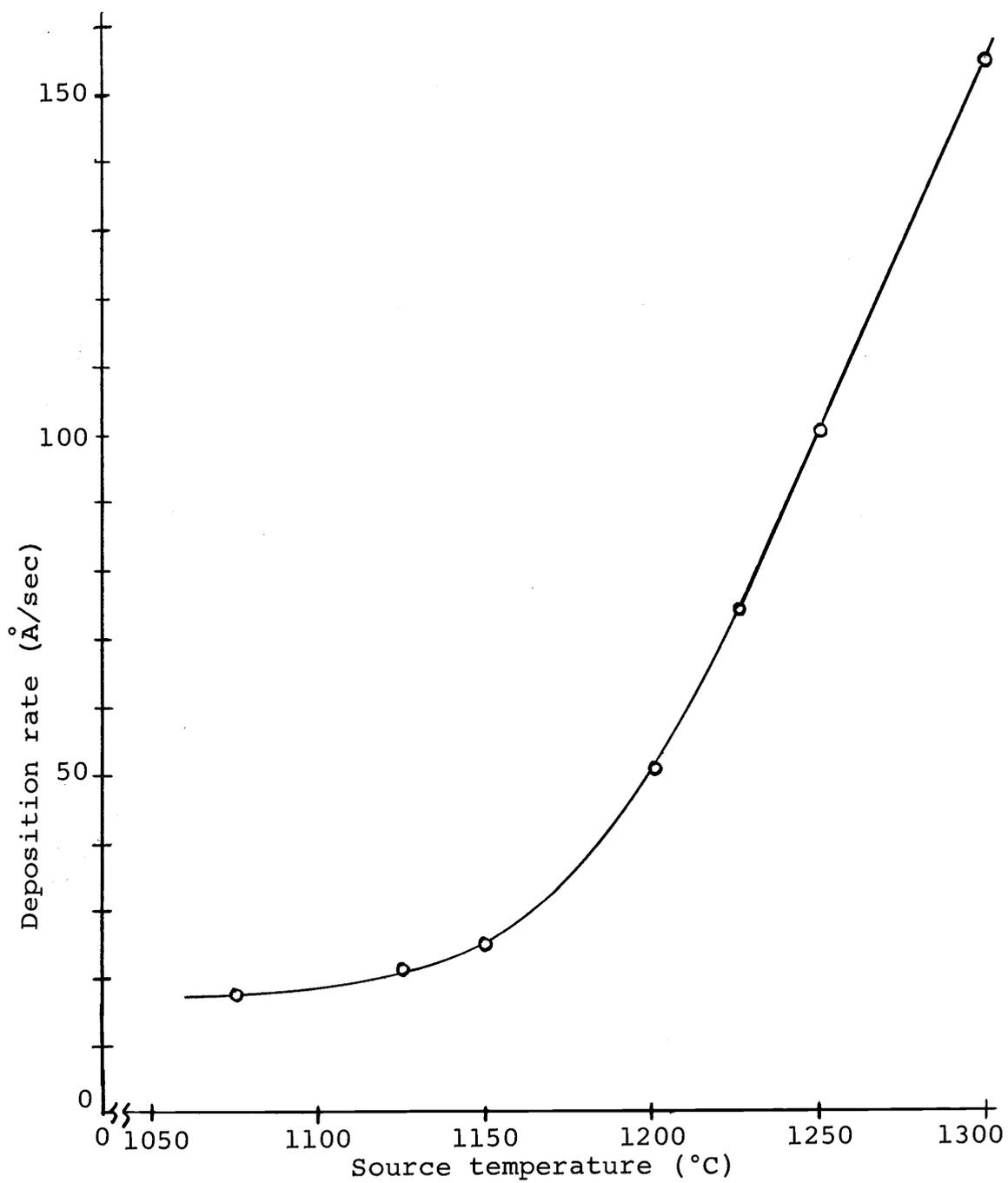


Figure 9. Deposition rate versus source temperature at a source-substrate distance of 5.1 inches and at the bell jar pressure of  $4 \times 10^{-6}$  mmHg.

distinguishing feature of the films. Whereas the films evaporated under poor vacuum condition ( $\sim 1 \times 10^{-4}$  mmHg) and deposition rate  $\leq 10 \text{ \AA}/\text{sec}$  with substantial oxygen and water vapor resulted in a light yellowish to colorless appearance characteristic of quartz ( $\text{SiO}_2$ ) indicating a large extent of oxidation and resultant mixture of SiO,  $\text{SiO}_2$  and an intermediate oxide  $\text{SiO}_x$  (4, p. 8; 16, p. 273), where  $1 < x \leq 2$ . This suggests the intermediate oxide  $\text{SiO}_{1.5}$ , or  $\text{Si}_2\text{O}_3$ .

In general the evaporated films can be a composite of Si, SiO,  $\text{SiO}_2$  and  $\text{Si}_2\text{O}_3$  depending on the evaporation condition. However, a literature search revealed no method of determining the percentages of Si, SiO,  $\text{Si}_2\text{O}_3$  and  $\text{SiO}_2$  in an evaporated thin film sample (16, p. 273). But since Si and SiO are strong absorbers in the uv and visible regions, it was felt that the optical properties could be used as a measure of the relative compositions of the films.

The effects of pressure and deposition rate on the optical properties of the films are discussed in the next section.

## VII. TRANSMISSION SPECTRA OF THE FILMS

A. Experimental Setup

Two setups were used to measure the transmission spectra. The first setup used the following equipment:

Tungsten light source B&L 33-86-39 -- spectrum from 3000 Å to far infra-red.

Monochrometer B&L 33-86-66

Photomultiplier tube RCA 931 A

Electrometer Keithley Model 602

The first setup for measurement of transmission spectrum is shown in Figure 10.

Procedure:

1. A blank glass and a substrate with SiO deposited on it were loaded on two sample holders. The former will be used as a reference.
2. The distance between the light source and the entrance slit was adjusted so that the photomultiplier tube did not saturate and the output on the electrometer gave optimum sensitivity through the range of interest.
3. The wavelength was then dialed on the monochrometer.
4. The SiO sample and the reference sample were put alternately at the entrance slit and the output readings were recorded from the electrometer.

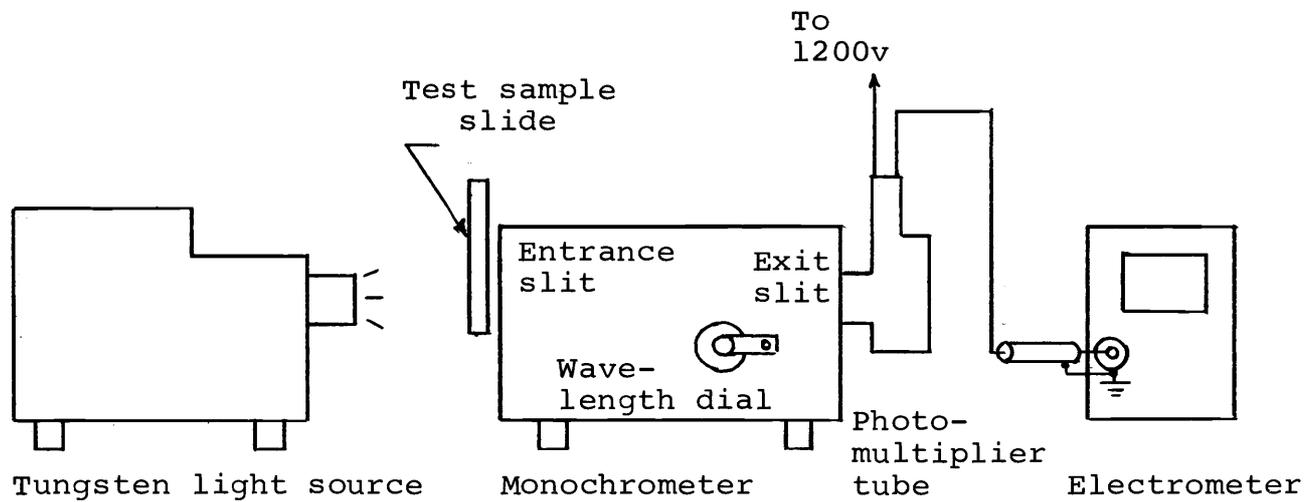


Figure 10. Experimental setup #1 for measurement of transmission spectrum.

5. The above step was repeated in the range of uv through part of the visible (from 3500 Å to 6800 Å).

The transmission (or transmittance) of the SiO film was obtained by dividing the SiO sample output by that of the reference glass. This ratio is the ratio of transmitted light to the incident light provided the sample substrate glass and the reference glass transmit the same amount of light, and the light source intensity stays approximately constant. These conditions hold for practical purposes.

The second experimental setup to measure transmission spectra of the SiO films was a Perkin-Elmer Model 450 NIR Spectrophotometer. This instrument made possible a direct recorder plot of sample transmittance relative to the reference glass versus wavelength.

The setup and block diagram of the principle of operation are given in Figure 11 and Figure 12.

Since a comparison of the results obtained on these two setups agreed with each other, the second setup was used on subsequent measurements.

#### B. Spectral Transmission of Evaporated Films of Different Thicknesses

It was mentioned in a previous section that the composition and consequently the optical properties depend on the deposition rate and residual pressure during

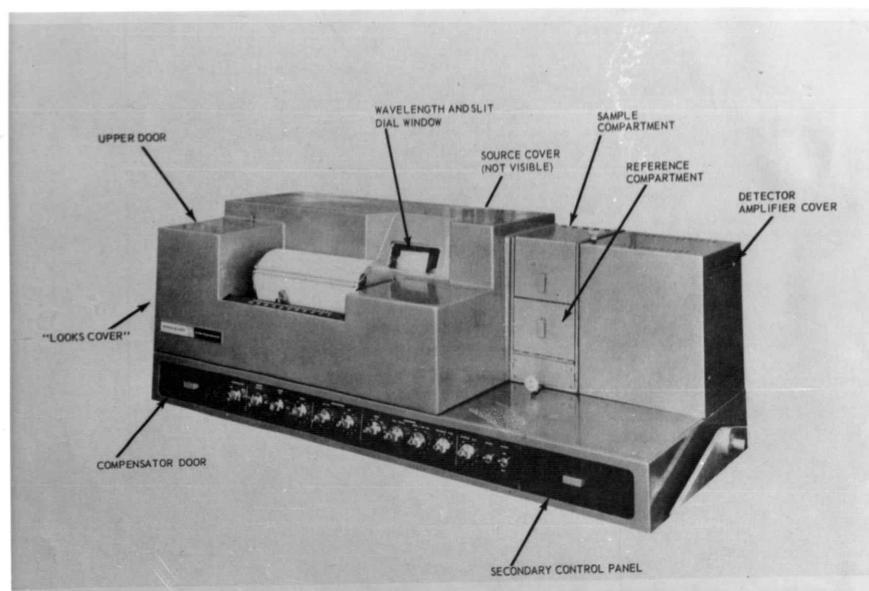


Figure 11. Perkin-Elmer Model 450 NIR Spectrophotometer.

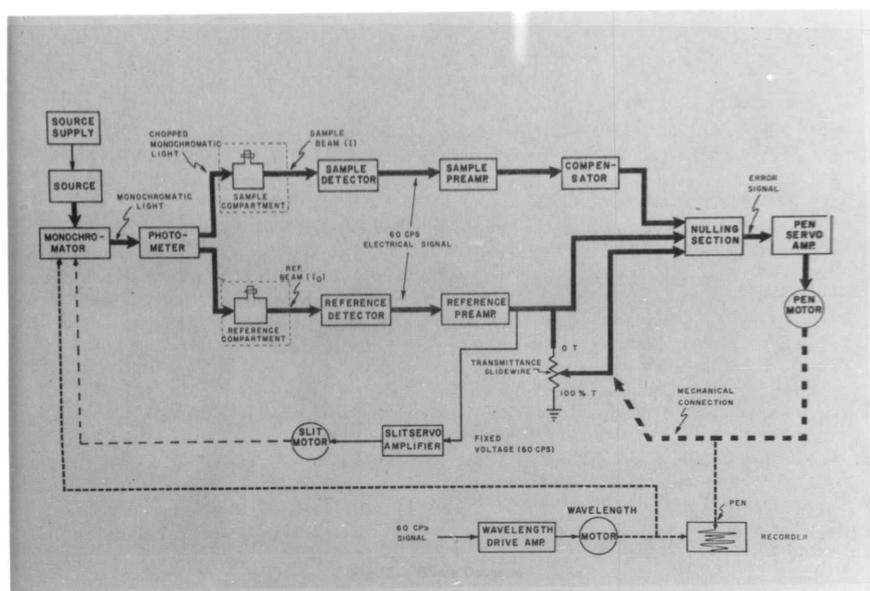


Figure 12. Block diagram of Model 450 NIR Spectrophotometer.

evaporation.

Transmission spectra of two sets of films of different thicknesses are shown in Figure 13 and Figure 14; one set evaporated at  $\sim 4 \times 10^{-6}$  mmHg and deposition rate of  $\sim 16 \text{ \AA}/\text{sec}$  and source temperature of  $\sim 1075^\circ\text{C}$ ; the other set of films evaporated at  $\sim 1 \times 10^{-4}$  mmHg, at deposition rate  $\leq 10 \text{ \AA}/\text{sec}$  and source temperature of  $\sim 1075^\circ\text{C}$ .

It is evident that films deposited at low pressure and fast deposition rate exhibit strong absorption in the uv through the blue end of the visible spectrum. The absorption increases with thickness of the film. The spectral sensitivity of photoresist AZ 1350 showed it to be most sensitive to lights of wavelengths up to  $4500 \text{ \AA}$  (1, p. 450). Films of thickness from  $\sim 9650 \text{ \AA}$  to  $\sim 18,600 \text{ \AA}$  ( $\sim 9650 \text{ \AA}$  to  $\sim 13,500 \text{ \AA}$  is optimum) transmit less than 15% of the light up to  $4500 \text{ \AA}$  and yet are semi-transparent, and may be used as see-through masks. The absorption of uv light in the films is the basis for using SiO films as masking material.

The strong uv absorption together with the characteristic brown color indicate a predominance of SiO in the films with very little SiO<sub>2</sub>. Si in the film is unlikely because Si occurs due to disproportionation of source material from an excessively heated source above  $1350^\circ\text{C}$  (4, p. 8).

The films deposited at high pressure

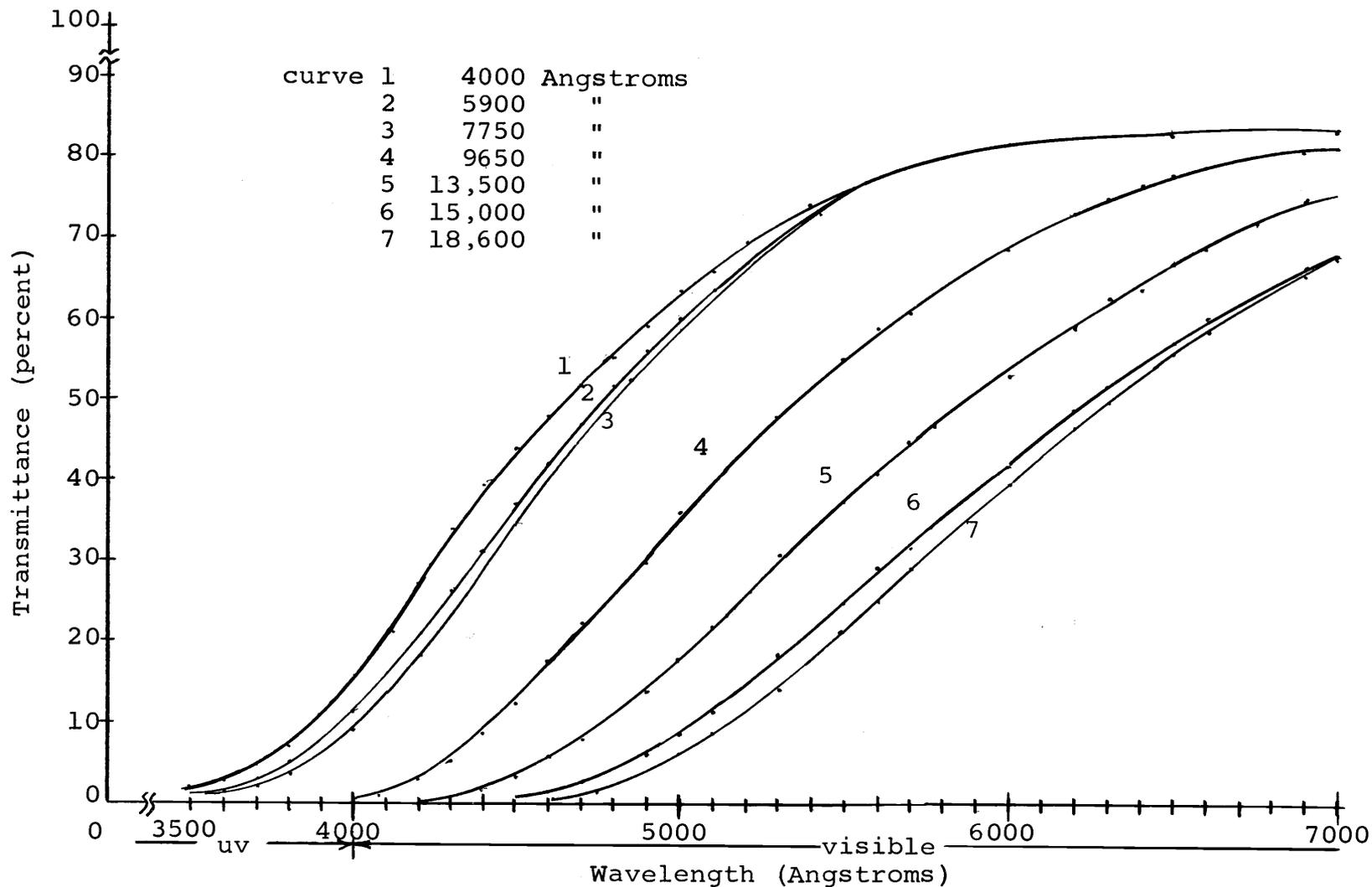


Figure 13. Transmission spectra of films of different thicknesses evaporated at  $\sim 4 \times 10^{-6}$  mmHg and deposition rate of  $\sim 16$  Å/sec.

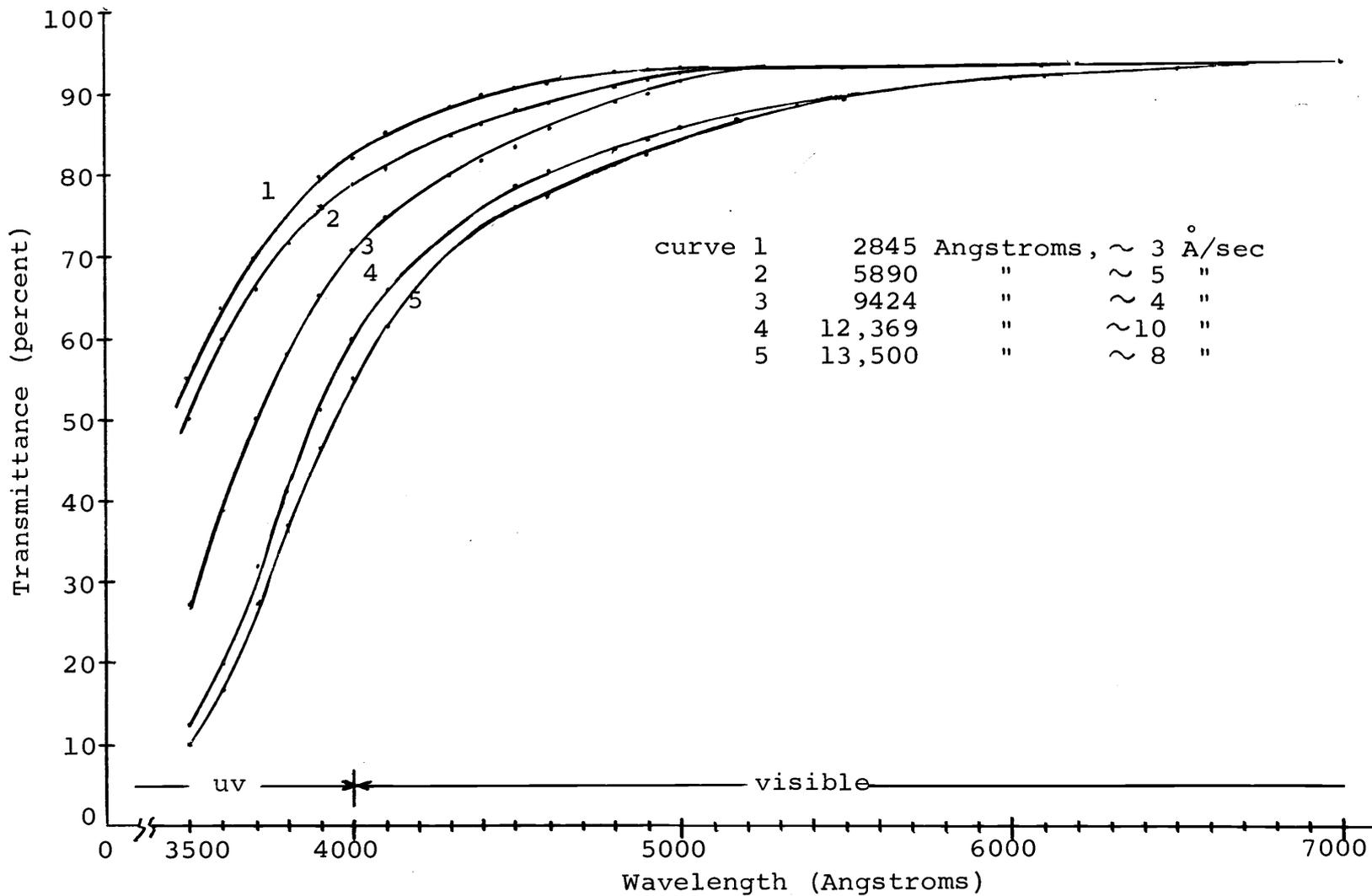


Figure 14. Transmission spectra of films of different thicknesses evaporated at  $\sim 1 \times 10^{-4}$  torr and deposition rate of  $\leq 10$  Å/sec.

( $1 \times 10^{-4}$  mmHg) and slow deposition rate ( $\leq 10 \text{ \AA}/\text{sec}$ ) showed little uv and visible absorption. If the films were evaporated under high pressure (up to  $\sim 5 \times 10^{-4}$  mmHg) at extremely slow deposition rate ( $\sim 1 \text{ \AA}/\text{sec}$ ) then the resultant films would exhibit the characteristic of pure  $\text{SiO}_2$  (6, p. 185) with virtually no absorption in the uv and visible. However, since the films did show some absorption in the uv and visible, this suggests the films to be a mixture of  $\text{SiO}$ ,  $\text{SiO}_2$  and  $\text{Si}_2\text{O}_3$  (4, p. 8; 16, p. 273). The absorption increases with film thickness since the content of  $\text{SiO}$  increases with thickness. The films are characterized by a light brown to transparent color.

The experimental results confirm the findings of a number of investigators that the composition of silicon monoxide films is dependent upon the deposition rate and the total pressure in the system.

In general the chemical composition of the film is usually a composite of  $\text{Si}$ ,  $\text{SiO}$ ,  $\text{Si}_2\text{O}_3$  and  $\text{SiO}_2$ . The predominance of one component over the others is a function of source temperature, deposition rate and residual gas pressure during evaporation, and there is no method to determine the exact composition of each component.

For our purpose, close-to-true  $\text{SiO}$  films deposited under low pressures were investigated and used to make masks.

## VIII. EXPOSURE TEST OF LIGHT THROUGH THE SiO FILMS

A. Experimental Setup

## Equipment:

Automatic timer

Tungsten light source -- Sylvania DWY sun gun bulb

Purpose:

The purpose of this test was to determine the uv light blocking properties of evaporated SiO films of different thicknesses.

A tungsten light source was used and the exposure time was determined for light to pass through the SiO film and expose the photoresist AZ 1350 on a silicon wafer underneath the film.

A high resolution plate with a pattern of opaque lines with a width of 0.5 mm was used in conjunction with the SiO plate, which had a uniform coating, to determine the masking efficiency of the SiO film.

The pattern plate was set on top of the SiO plate. The combination was exposed with the tungsten light at a distance of 16 cm onto a wafer coated with photoresist AZ 1350 for a certain exposure time. The wafer was developed and then examined by inspection under the microscope.

If not enough light passed through the SiO film, no clearly defined pattern developed; thus the SiO film blocked the light that came through the top plate which

had the pattern on it.

The exposure time was successively increased until a discernible pattern developed on the wafer indicating enough uv light passed through the SiO film and exposed the photoresist AZ 1350. The above steps were repeated for films of different thicknesses.

#### B. Result of Light Exposure Through SiO Films of Different Thicknesses

Exposure times were tested from four seconds, which is the exposure time for normal photomasking procedure, up to the mask failure limit for exposure through the SiO films.

The various exposure times for films of different thicknesses are listed in Table III.

The mask failure time is the time of exposure required to develop clearly visible patterns on the wafer. The optimum exposure time is the time interval that no discernible patterns developed on the photoresist.

It can be seen from Table III that optimum exposure time can be increased as the film thickness increases. Films of thickness from 9650 Å to 15,000 Å are best for use as masks since they have longer optimum exposure time than the 5900 Å and 7750 Å films. Although the normal exposure time for photomasking is four seconds, a film 9650 Å thick can block uv light up to six seconds without exposing

photoresist on the wafer. A 15,000 Å film would stand up to nine seconds. Therefore, films of thickness from 9650 Å to 15,000 Å provide a safety margin in photomasking yet are still semitransparent.

## IX. PROPERTIES OF THE SiO FILM RELATING TO USE AS MASKS

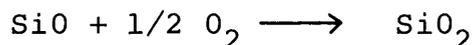
### A. Mechanical Properties, Amenability to Scratching and Repeated Cleaning

Such properties as mechanical stress, stability, susceptibility to scratching and amenability to repeated cleaning are of interest in the use of SiO as masking material.

It was shown by Priest (11, p. 301) that mechanical stress is a major cause for peeling, buckling and cracking. But at pressure  $\sim 5 \times 10^{-6}$  torr and evaporation at source temperature between 1300° and 1400°C, film stress should be minimum.

To be useful as masks the film should not be susceptible to scratching. A scribe was used to scratch the films, and qualitatively, it appeared that SiO was less easily scratched than the emulsion material used for high resolution plates.

Mechanical stability is a direct function of the composition of the material. On oxidation SiO turns into SiO<sub>2</sub> by the following reaction:



thus increasing in volume and changing dimension. However, it has been shown that SiO films evaporated under good vacuum conditions ( $\leq 10^{-5}$  mmHg) and fast deposition rates ( $> 10 \text{ \AA}/\text{sec}$ ) oxidized very little upon exposure to air

(6, p. 181) and even much less with time. The dimensional stability was probably negligible for practical considerations.

Repeated cleaning with acetone and DI water did not damage the film provided the film adherence was good and there was no cracking or peeling.

#### B. Resolution Obtained on the Silicon Wafer

A dark field SiO mask and a light field SiO mask, both of 9650 Å thickness, deposited at pressure of  $\sim 4 \times 10^{-6}$  mmHg, deposition rate of  $\sim 16$  Å/sec and a source temperature of  $\sim 1075^\circ\text{C}$ , were used to determine the resolution obtained on the silicon wafer.

The resolutions that were obtained on the silicon wafer from the dark field SiO mask and the light field SiO mask are shown in Figure 15 and Figure 16. The exposure time on the wafer was four seconds. It can be noted from these figures that lines or spaces of a width of  $\sim 3$  to 5 microns were obtained.

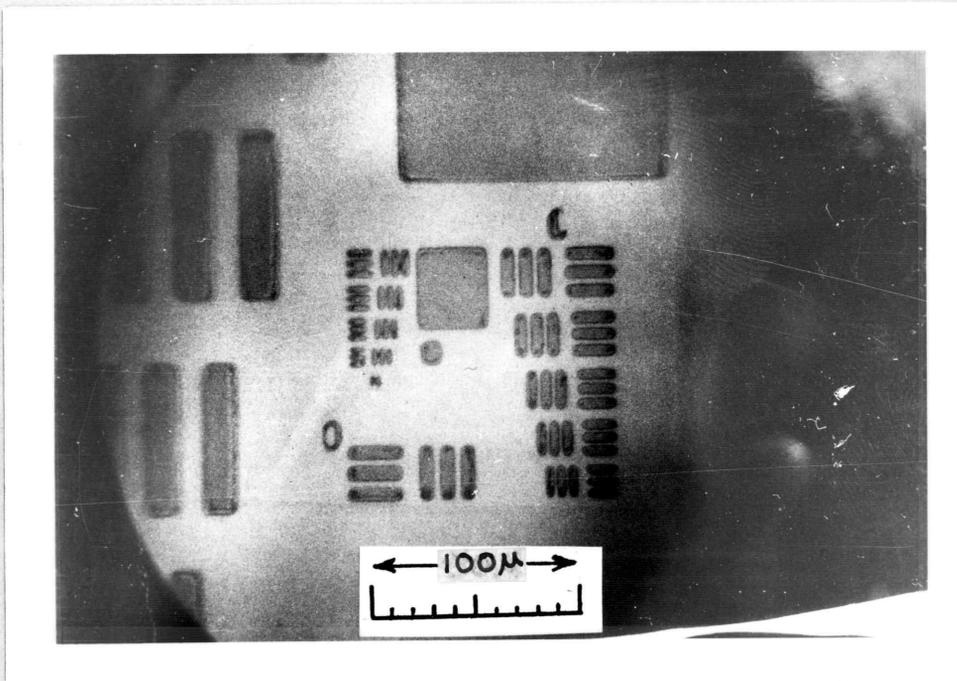


Figure 15. Resolution obtained on wafer from the dark field SiO mask.  
(Dark area is photoresist; clear portion is silicon substrate)

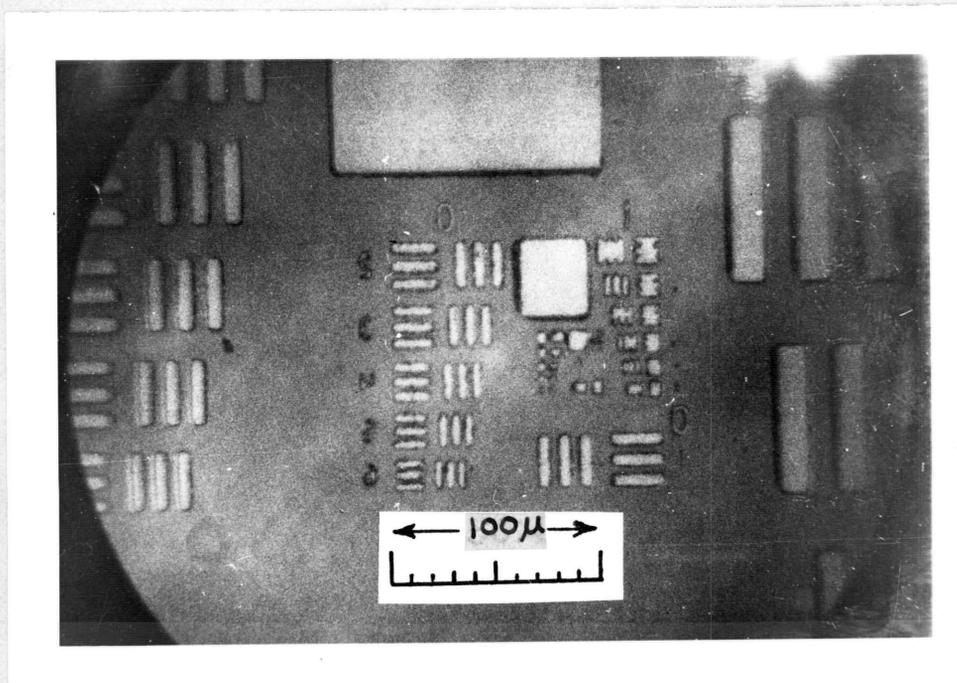


Figure 16. Resolution obtained on wafer from the light field SiO mask.  
(Dark area is photoresist; clear portion is silicon substrate)

## X. SUMMARY AND CONCLUSIONS

From results of the foregoing sections it was found that the Lift-off Process produced SiO mask pattern with  $\sim 2.5$  microns resolution. The resolution obtained on the silicon wafer was  $\sim 3$  to 5 microns.

The Exposure Test showed that SiO films of thicknesses from  $9650 \text{ \AA}$  to  $15,000 \text{ \AA}$  ( $9650 \text{ \AA}$  to  $13,500 \text{ \AA}$  is optimum) could mask enough light in the uv and visible range to be useful as masks and yet were semitransparent. The Measurement of Transmission Spectrum showed that SiO films from  $\sim 9650 \text{ \AA}$  to  $18,600 \text{ \AA}$  thick deposited at pressure of  $\sim 4 \times 10^{-6}$  mmHg, deposition rate of  $\sim 16 \text{ \AA/sec}$ , source temperature of  $\sim 1075^\circ\text{C}$  and source-substrate distance of 5.1 inches, exhibited strong uv absorption extending into the visible region.

The resistance boat evaporation method proved useful and practical for several deposition runs. The source temperature ( $\sim 1075^\circ\text{C}$ ), deposition rate ( $\sim 16 \text{ \AA/sec}$ ) and pressure ( $\sim 4 \times 10^{-6}$  mmHg) can be controlled to produce an SiO film with the desired uv absorption properties.

The substrate cleaning procedure was adequate for good film adherence.

All the above results point to the feasibility of using SiO films to make see-through masks. However, this entailed additional processing steps in making conformal

masks from existing ones. This is equivalent to making a negative of the mask pattern and consequently reversing the procedure of generating artwork (window areas should be light instead of dark for positive photoresist AZ 1350). Subsequent steps were evaporation and photoresist stripping.

It has been found that at source temperature between 1300° and 1400°C SiO films with minimum mechanical stress can be deposited (11, p. 302). However, at source temperatures of 1300° to 1400°C high evaporation rates may cause spitting and result in a film less dense and with many pinholes.

The resolution obtained on the SiO mask was approximately 2.5 microns per line or space and 3 to 5 microns per line or space on the silicon wafers.

Some peeling and poor definition of elements shown in the resolution photographs of the masks were probably due to the fact that these films were produced at source temperature of approximately 1075°C. At such low temperatures the deposited film contained large amounts of stress, thus buckling, peeling and cracking were not uncommon (4, p. 946; 11, p. 302). The stress in the film can be removed somewhat by heating the substrate during evaporation or annealing the film at 250°C after deposition (12, p. 279).

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## APPENDIX

Table I. Oxide Film Thickness versus  
Deposition Time.

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Pressure =  $4.0 \times 10^{-6}$  torr  
Source-substrate distance = 5.1 inches

Sample No.	Source Temp. (°C)	Deposition Time (min.)	Fringe Displacement (No. Fringes)	Oxide Thickness (Å)
1	1150	1.5	0.42	2250
2	"	3	1.52	4500
3	"	4.6	2.38	7000
4	"	6.4	3.23	9500
5	"	10	5.0	14,750
6	1250	0.4	0.85	2500
7	"	1.0	2.04	6000
8	"	1.6	3.3	9750
9	"	2.4	4.95	14,500
10	1075	2.0	0.69	2050
11	"	4.0	1.36	4000
12	"	6.0	2.01	5900
13	"	8	3.16	7750
14	"	10	3.27	9650
15	"	12	3.98	11,700
16	"	14	4.59	13,500

---

Table II. Deposition Rate versus Source Temperature.

Source-substrate distance = 5.1" Pressure = $4.0 \times 10^{-6}$ torr					
Sample No.	Source Temp. (°C)	Deposition Time (min.)	Fringe Displacement (No. Fringes)	Oxide Film Thickness (Å)	Deposition Rate (Å/sec)
1	1075	6	2.05	6000	16.6
2	1125	2.0	0.86	2520	21
3	1150	6.4	3.3	9500	24.6
4	1200	2	2.05	6000	50
5	1225	2	3.05	9000	75
6	1250	1.6	3.32	9750	101
7	1300	2.0	6.3	18,600	155

Table III. Exposure Time versus SiO Film Thickness.

Source-substrate distance = 16 cm Light source = tungsten			
Sample No.	Film Thickness (Å)	Mask Failure Time (sec.)	Optimum Exposure Time (sec.)
1	5900	7	4~5
2	7750	9	4~5
3	9650	10	4~6
4	11,700	12	4~7
5	13,500	13	4~8
6	15,000	15	4~9