1.0

1.1

1.25

4.5
5.0
5.6

2.8

3.2

3.6

4.0

2.5

2.2

2.0

1.8

1.4

1.6

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

AD A093450

LEVEL II

AN ULTRASENSITIVE ELECTRON (SOFT X-RAY) SILVER HALIDE/
CHALCOGENIDE NEGATIVE OR POSITIVE INORGANIC RESIST.

Annual rept. no 1, 10 Sep 79 - 15 Oct 80,

Jerome M. Lavine
Ionomet Company, Inc.
1660 Soldiers' Field Road
Brighton, MA 02135

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10 November 1980

First Annual Report, 10 September 1979 - 15 October 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have successfully Ag-photodoped As_2S_3 using photographic Ag derived from evaporated AgBr. The use of evaporated AgBr has resulted in a 1000-fold increase in speed. We have shown that evaporated AgBr has very high sensitivity in the deep UV (50 microJ/cm² at 2600Å), at soft x-ray wavelengths (5 microJ/cm² at 7Å) and confirmed the previously observed e-beam sensitivity of 10^{-9} coulombs/cm². We have shown the feasibility of using evaporated AgBr as the photon sensitive layer of a multi-layer photoresist system for sub-

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20. micron lithography.

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I. INTRODUCTION

A. Background

In 1964 Tubbs and Forty[1] first reported the photographic properties of a thin film of PbI_2. Extending this work on films, Kostyshin and his coworkers[2] determined the photographic sensitivity of a large number of semiconducting and insulating materials in 1966. Among the sulfides reported was As_2S_3. Kostyshin further noted that such films were more sensitive when deposited on a metal substrate. In 1971 Inoue and his co-workers[3] described the Ag photodoping of chalcogenide glasses and later showed that negative relief images could be obtained by their techniques.[4] In 1976 Yoshikawa et al[5] first suggested the use of such systems as a novel photoresist. The Ag photodoping of As_2S_3 to produce negative relief images is accomplished in the following way: An amorphous film of a chalcogenide such as As_2S_3 is deposited by evaporative techniques and a thin film of Ag is deposited on top of the As_2S_3. The sample is appropriately masked and exposed to bandgap radiation. In the region of exposure, the Ag migrates into the As_2S_3. After exposure, Ag remaining on the surface is removed with an Ag etchant. Then an alkaline etch is used to remove the As_2S_3 in the unexposed areas. The main drawback of this process, and one of the reasons for its discovery, is that the Ag will diffuse into the As_2S_3 in the dark at room temperature. It remained for Chang and his coworkers[6] to suggest that AgCl evaporated on the surface of the As_2S_3 would provide Ag for photodoping, but only in the presence of radiation. It was our suggestion[7] that evaporated AgBr would provide a better source of Ag for the photodoping process, and that, if the images

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were developed as in the conventional photographic process, the sensitivity of the system could be vastly increased from the 1 J/cm^2 observed for metallic Ag.

The objective of our proposal for the first year of our contractual work was to show the feasibility of this concept, to define some of the parameters, to assess the sensitivity of this system to deep UV, e-beam, ion-beam, and x-ray radiation, and to assess the potential of such a composite inorganic system as a microlithographic resist.

B. Ag Photodoping Models

Goldschmidt and Rudman[8] have explained the Ag photodoping of As_2S_3 as a three part process. The first part requires a critical radiation damage of the As_2S_3; the second, a photon-assisted activation of the Ag; the third, which proceeds with a square root of time dependence, has been considered as a diffusion process. Kokado, Shimizu, and Inoue[9] have also proposed a similar model. Malinowski[10] has preferred to describe the situation in chemical terms and has called the reaction a tarnishing reaction.

There is considerable experimental evidence that during illumination, even in the absence of Ag, there is a rearrangement of the bonding of the chalcogenide, as evidenced by the fact that the optical absorption is shifted to longer wavelength, the refractive index and the solubility in certain reagents is altered, and there is a decrease in film thickness.

These effects have been used for photographic imaging with the chalcogenides alone. With the inclusion of Ag the changes become more profound. In the latter stages of the reaction compounds of Ag/As/S have been observed and, when the amount of Ag is sufficient,

an Ag_2S phase is formed. Malinowski postulates that the conductivity plays a prominent role. Initially, the conductivity of the chalcogenide is extremely small. Due to illumination, and especially with the inclusion of Ag, the conductivity increases. With the increased conductivity not only Ag^+ but electrons as well can transfer through the exposed region. Mobile S^- species reaching the Ag layer are permanently trapped due to chemical bonding of Ag and S. Although further progress tends to be blocked by the space-charge thus established, additional Ag^+ transfer to this layer and build up an Ag_2S layer. This phase of the reaction proceeds fairly rapidly. In order to account for the quadratic time dependence of the third phase, Malinowski postulates a thickening of the Ag_2S layer at a rate proportional to the square root of time as proposed by Wagner for many chemical reactions. The failure of Ag to diffuse laterally outside of the illuminated region may be understandable on the basis of short-lived S^-. However, some features of Malinowski's model are less than appealing. The presence of Ag at very large depths, of the order of 20 microns, and the lack of Ag to form a substantial thickness of Ag_2S are all somewhat difficult to accept with his model. We have confirmed that Ag_2S does indeed form on the surface. We have perfomed etching experiments which, upon removal of the initially formed layer of Ag_2S, preclude any substantial photodoping. Therefore, the formation of a Ag rich phase at the surface under illumination does not contravene our experiments.

However, the work of Buroff et al[11] suggests that there may be no more than a saturated surface concentration of Ag at the surface driving a diffusion mechanism. The only measurement of the diffusion coefficient of Ag in As_2S_3 was done in the dark and suggested

-3-

values that would yield negligible penetration even if there were some localized heating due to the illumination. For our purposes, we have thought about the Ag photodoping as a system with two diffusion coefficients, one in the dark and one in the illuminated region. In the illuminated region the lattice changes provide an avenue for high speed Ag^+ motion. Since the one measurement of the diffusion coefficient suggested an enhancement in the presence of an electric field, we think that the assumption of Ag^+ diffusion may be justified. In the photographic literature it is well accepted that Ag^+ is a very mobile ion. The mechanism of Ag photodoping obviously requires additional investigation.

II. EXPERIMENTAL

A. Evaporations

1. AgBr Evaporations

We have dedicated an NRC 6" diffusion pumped system to AgBr evaporations. The system utilizes dinonyl phthalate as the pump oil. The system has been jigged and fixtured to allow for a variety of experiments. We have evaporated from 6" W boats, from W-heated Al_2O_3 crucibles, and from SiO_2 crucibles with Ta heaters. We observe little difference due to the variety of boats, the significance being mainly in film deposition parameters. The system is shuttered and monitored by an Inficon thickness monitor. AgBr films are routinely deposited upon substrates of subbed glass, As_2S_3, and subbed Si wafers. During this period we have made over 300 evaporations of AgBr. Evaporations are performed at nominal boat temperatures of the order of 675°C resulting in deposition rates of the order of 25 Å/sec. Thicknesses in the range of 1500 - 2500 Å are typically used. We routinely check

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the optical sensitivity of our AgBr films on subbed glass substrates, employing an EG&G Sensitometer with flash exposure (Xenon) of 2×10^{-5}, 2×10^{-4}, and 1×10^{-3} J/cm^2 on each of three ranges. The sensitivity is measured using a Kodak #2 step wedge. Figure 1 shows a plot of AgBr sensitivity as a function of the thickness of the AgBr film. Each step of the abscissa is a factor of the square root of 2 in sensitivity.

AgBr films are particularly sensitive to contaminants and impurities. In order to achieve the high sensitivity we observe it is essential that the starting material be properly purified. It is also important to employ the right diffusion pump oil and to maintain cleanliness in the vacuum system. Failure to observe proper procedures can result in poor sensitivity and in fogging. We have early learned that the presence of As_2S_3 samples in the vacuum system during the AgBr evaporation reduces the sensitivity of AgBr films on any substrate by about one order of magnitude. This is also shown in Figure 1.

2. AgCl

We have similarly evaporated AgCl for a variety of experiments. Evaporation was performed at temperatures of the order of 670°C in times (rates) similar to that employed with AgBr. We have made about 20 runs of AgCl for a variety of doping experiments.

3. AgBrI

In order to decrease grain size (as we shall describe below), we have added 3 molar percent of AgI to our charges of AgBr. Evaporation rate is roughly one-third to one-quarter the rate for AgBr. We have made about 50 runs of AgBrI. These samples were used in photodoping experiments, for evaluation of grain size reduction, and mostly for resolution experiments.

KODAK #2 STEP WEDGE OPTICAL DENSITY

(Each step $2^{1/2}$ in optical density)

AgBr evaporated with no As$_2$S$_3$ present

with As$_2$S$_3$ present

INFICON THICKNESS, ANGSTROMS
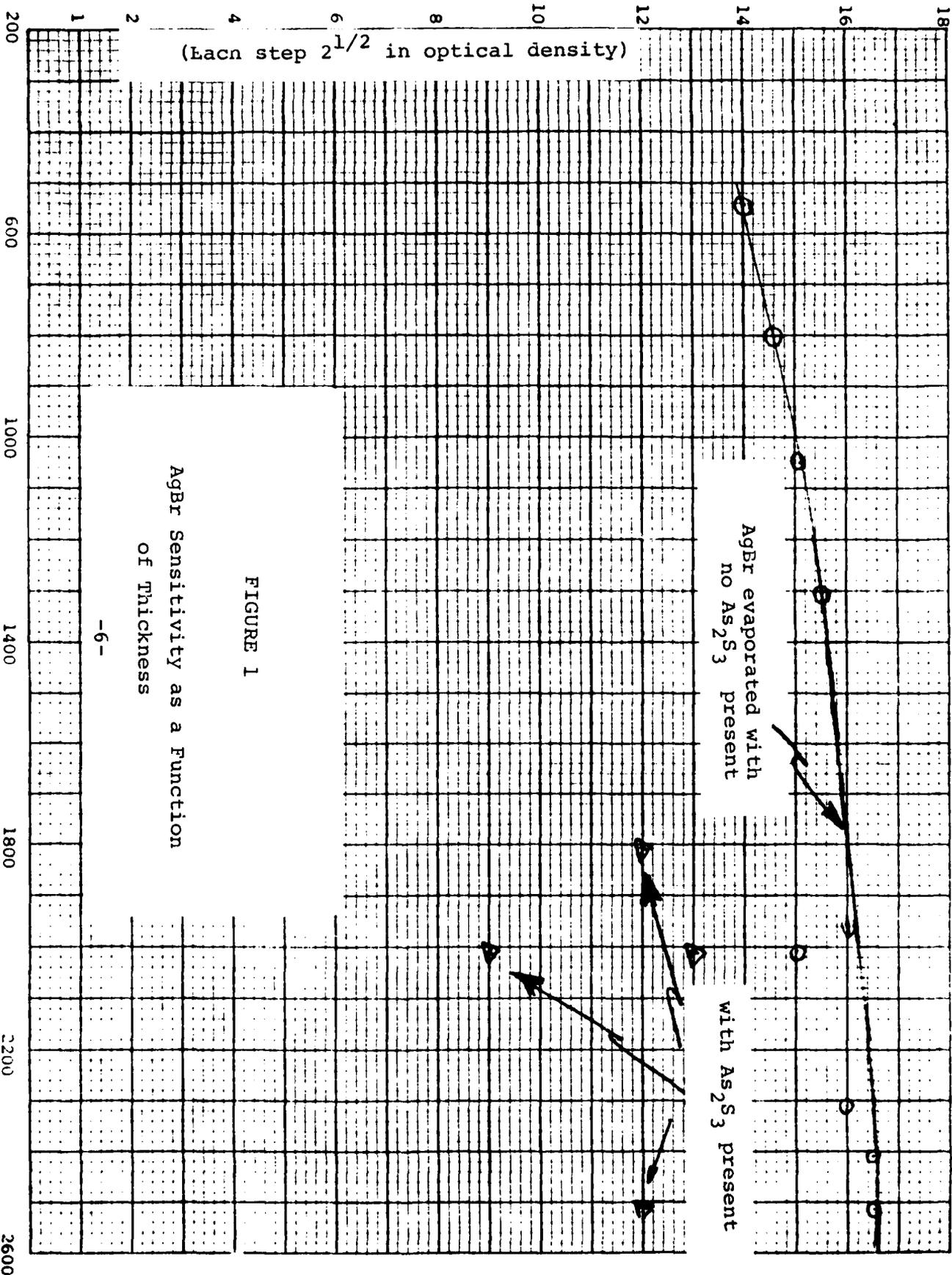
FIGURE 1

AgBr Sensitivity as a Function of Thickness

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4. As_2S_3

Because of the known contamination problem associated with this material, we have dedicated a 4" CVC diffusion-pumped system to As_2S_3 evaporations. In this system we have found Octoil S acceptable as a pump oil. The As_2S_3 is evaporated at the relatively low temperature of approximately 300°C and with low deposition rate of about 100 Å/min. Total film thickness is typically 3000 Å. We have used two commercial sources of As_2S_3, Servofrax and Leico Industries. If the evaporation is done slowly, an amorphous film grows; if done rapidly, a crystalline film results. At 100 Å/min we always obtain an amorphous film. During this period we have made about 100 evaporations of As_2S_3.

5. Evaporations to Decrease Domain Size of AgBr

In order to decrease domain size we initiated a series of experiments. At first, recognizing the competition between nucleation and growth, we increased the evaporation rate. In an open crucible this led to both spitting and different AgBr properties. We then tried covered boats and baffled boats, equally unsuccessfully. Finally, by decreasing the source to substrate distance, we succeeded in increasing the rate of evaporation by at least a factor of four, ranging from 100 - 200 Å/sec. However, in evaporating AgBrI, we find that we must reduce our rate to about 25 Å/sec in order to achieve fog-free films. We have recently designed and built a substrate holder to cool our samples below room temperature. Experiments along this line are now under way.

B. Ag Photodoping

1. With Evaporated Ag

Our initial photodoping experiments were with pure Ag in order to test our As_2S_3 films and to test some elementary ideas about Ag

photodoping. We evaporated Ag layers at thicknesses ranging from several hundred Å to about 30 Å onto substrates consisting of 0.3μm of As_2S_3. We then made patterned contact prints using a Hg source with dominant 3000 - 4000 Å radiation. These exposures were made with about .5 - 1 J/cm^2. After exposure we removed the unexposed Ag (generally with difficulty) using etchants such as $K_3Fe(CN)_6$. Negative relief images were then obtained by etching the As_2S_3 in NH_4OH or NaOH. These preliminary experiments convinced us that our evaporated As_2S_3 films could be Ag-photodoped and that capping of the Ag-photodoped regions occurred. We also learned that it required very little photodoped Ag to cap a region of As_2S_3. Ag thickness of the order of 30 Å was used successfully and we are not yet certain that we could not have further reduced the thickness. However, the generally low speed of such Ag/As_2S_3 systems as well as the difficulties in removing the Ag from the unwanted areas either because of autodoping of Ag (in the absence of light) or because of autodoping during evaporation prompted us to move on to AgH photodoping.

2. Evaporated AgBr Employed in the Photographic Mode

We have successfully photodoped As_2S_3 with photographic Ag derived from AgBr layers 1000 - 3000 Å in thickness. Exposures have ranged from about 200μJ/cm^2 to about 2 mJ/cm^2. The variation in sensitivity stems from the variation in AgBr thickness and also from partial desensitization of AgBr evaporated in the presence of As_2S_3.

Our procedures are as follows:

A 2" x 2" glass plate .060" thick is coated with a subbing material such as gelatin or a proprietary polymer used on Ionomet

mass spectrometer plates to promote the adhesion of As_2S_3. The subbing may be dip-coated or spun-on. A 0.3μm thick layer of As_2S_3 is then evaporated at 100 Å/min from an Al_2O_3 crucible heated at about 300°C. After cool-down the sample is transferred to the AgH vacuum system where AgBr is evaporated from a W boat held at about 675°C. The thickness of the AgBr has ranged between 1000 and 3000 Å. The sample is then placed in an aligner for contact printing with an appropriate mask. The Hg source used emits about 20 mW/cm^2 between 350 and 470 nm. After exposure ranging from 200μJ/cm^2 to 2 mJ/cm^2 the sample is developed for one minute in a developer suitable for AgBr films and then fixed in a standard fixing solution (20 g thiosulfate in 1 liter of H_2O). The resulting Ag image is visible and then may be photodoped by flooding with Hg light for times as short as 2 mins. Figure 2 shows a block diagram of this process.

Figure 3 compares the speed of Ag-photodoping using evaporated Ag. On the same curve is shown the speed of an AgBr film evaporated on subbed glass with no As_2S_3 present in the vacuum chamber.

Figure 4 shows a photograph of a contact print made by this technique. This photograph at 160x was taken with blue transmitted light. The dark areas are green under the blue illumination and are regions of capped As_2S_3. The white areas are regions where the As_2S_3 has been removed.

An As_2S_3 image such as this forms a very useful mask when employed with a photoresist such as Shipley AZ. Figure 5 shows the optical transmission characteristics of one of our samples of As_2S_3. Superimposed is the region of sensitivity of Shipley AZ-1350. We have used a mask prepared by Ag photodoping and etching of As_2S_3 to expose Shipley AZ-1350 B successfully.

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Ag - HALIDE

As$_2$S$_3$

SUBSTRATE

COLLIMATED LIGHT
MASK

PHOTOGRAPHICALLY
PROCESSED TO
PRODUCE Ag

PHOTODOPED WITH
Hg WHITE FLOOD
LIGHT
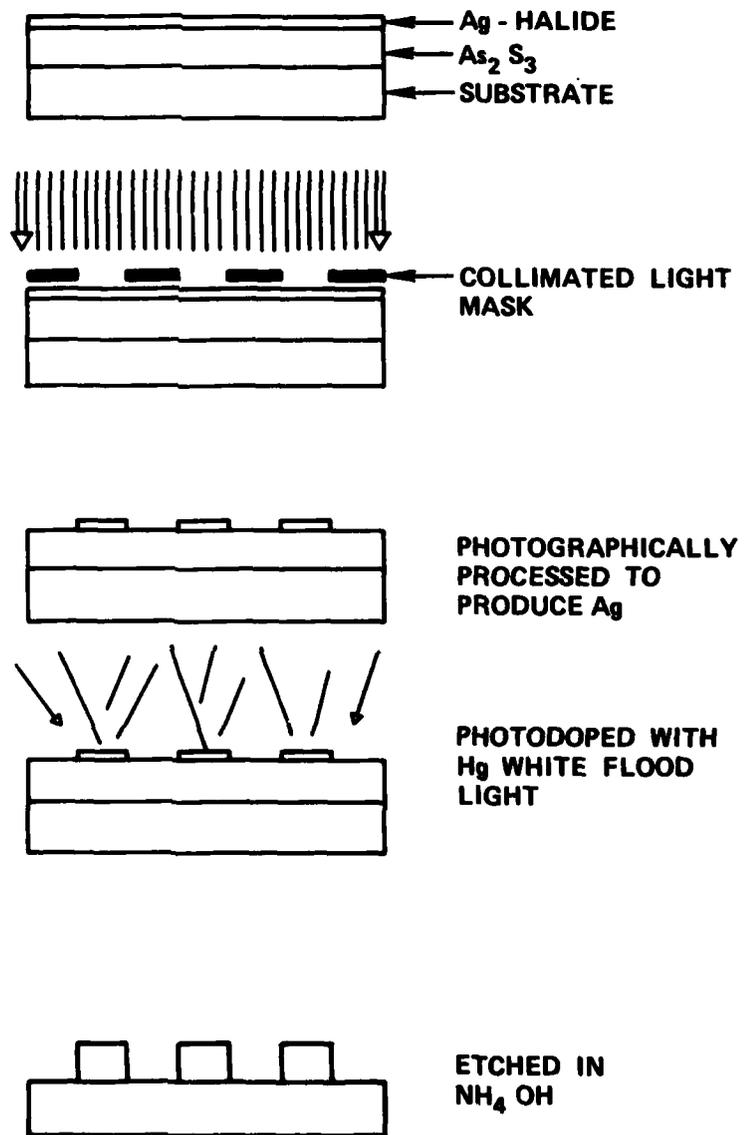
ETCHED IN
NH$_4$OH

FIGURE 2

Block Diagram of the Ionomet Process
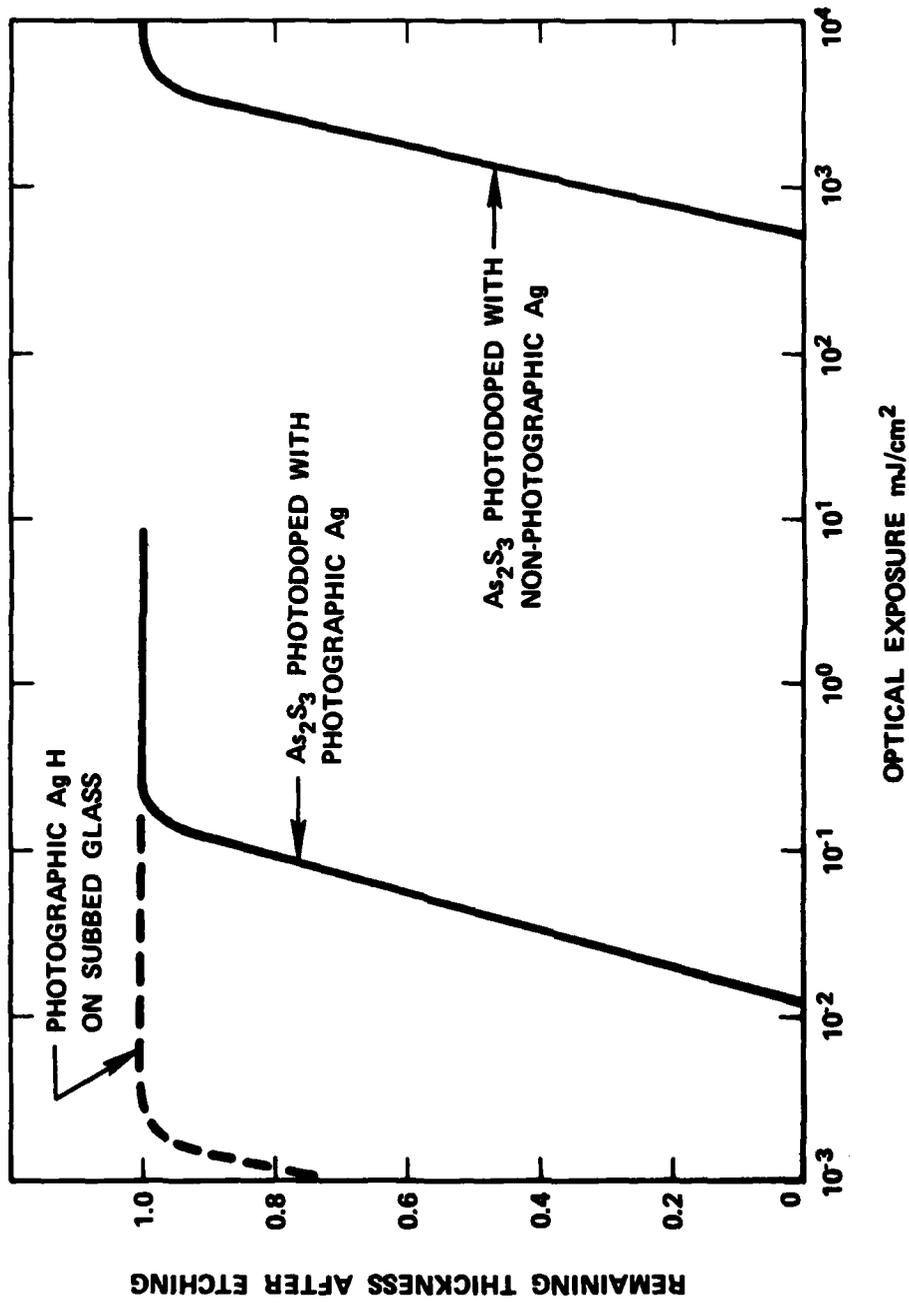
FIGURE 3

Comparison of the Speed of the
Ionomet Process with Metallic Ag
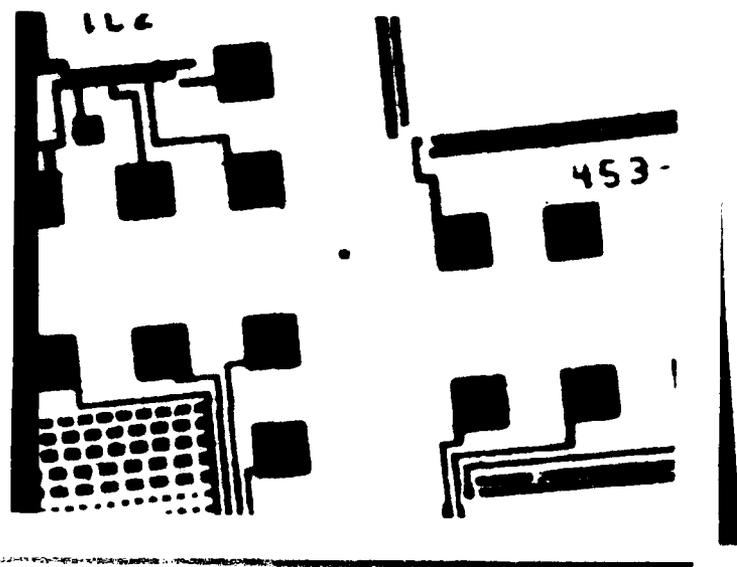Photodoping of As_2S_3

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FIGURE 4

A Photograph of Ag-Photodoped and Etched As_2S_3. Ag Derived
from Evaporated AgBr. (Photograph taken with blue transmitted
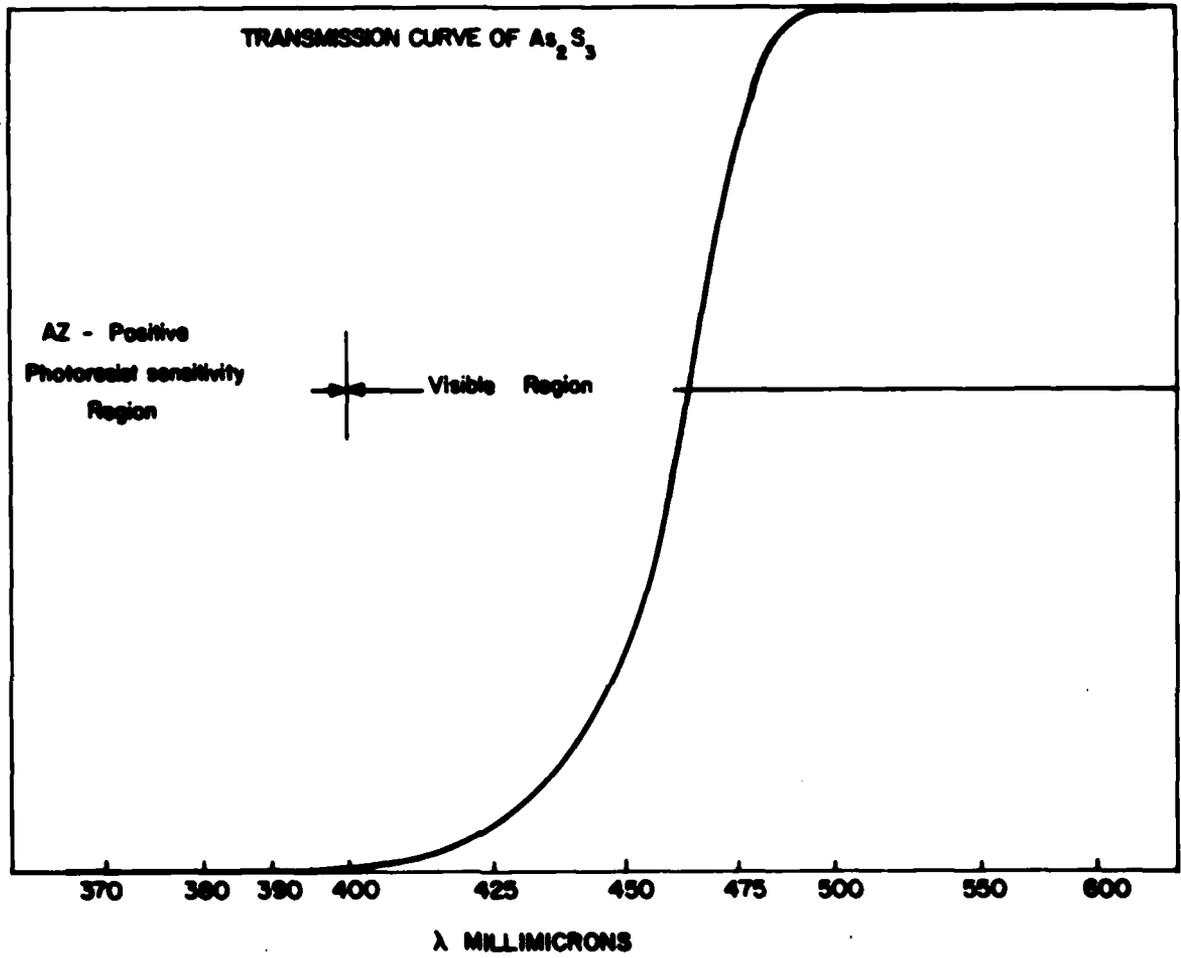light. Dark areas are As_2S_3 and appear green. These are capped
regions.) 160x.

FIGURE 5

Optical Transmission of 0.3 Micron Thick As_2S_3 Film

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3. With Evaporated AgCl

We have tried Ag photodoping at several thicknesses of AgCl. However, the development of these films has posed a problem. With our present capability we have been unsuccessful in controlling the speed of development of AgCl on As_2S_3, and the resultant images have correspondingly suffered. Therefore, after a broad-brush, short effort we abandoned any further attempts to use AgCl, in view of the fact that our main goals were not furthered by such an investigation.

4. With Aqueous $AgNO_3$

In the course of these investigations we have come to realize that perhaps as little as a few monolayers of Ag deposited upon the surface can have important consequences in altering the surface properties of As_2S_3. It is known that small quantities of free Ag may be deposited from a solution of $AgNO_3$, perhaps in a more controllable manner even than from a dilute Ag plating solution. We have used dilute concentrations, 10^{-2} molar $AgNO_3$, to deposit what we believe is a thin layer of Ag on top of the As_2S_3. Such procedures have been reported by Yoshikawa et al[12] on Se-Ge and by Buroff et al[13] on As_2S_3 with somewhat different results.

We have observed that dipping As_2S_3 in $AgNO_3$ for as little as 30 secs results in a capping action to the As_2S_3, in the absence of any radiation. Subsequent exposure of about 130 mJ/cm^2 does not alter the capping effect. Exposures longer than this result in loss of capping and in positive images. Yet, if the sample is first exposed to light for about an hour and then dipped in the $AgNO_3$, it is interesting to observe that even low energy exposures (of the order of 30 mJ) result in a negative image, provided that

we rinse in HCl. We believe that a combination of illumination plus Ag^+ results in Ag_2S which is insoluble in NH_4OH. However, dipping in HCl decomposes the Ag_2S and permits etching of As_2S_3 in NH_4OH.

5. Surface Sensitization

We have discovered a method of applying a very thin layer of Ag (or Ag/S) uniformly on the surface of As_2S_3. This process involves the deposition of a layer of evaporated AgBr with subsequent dipping into a reducing and a complexing agent for the Ag ion. Concentrations and times are adjusted to provide a final Ag level between 5 and 10 atomic layers. The Ag is probably present as the element but it may also exist in sulfide form since our analytical procedures will not differentiate between the two. The simple procedure for obtaining negative relief images is shown in Figure 6. In this case, exposures greater than about 150 mJ/cm^2 also bring about a reversal effect. This behavior is illustrated in Figure 7 which compares the speed of the several processes we have here described.

C. Spectral Sensitivity of Evaporated AgBr

We recognize that Ag photodoping of As_2S_3 proceeds most rapidly with bandgap photons as has been shown by Kokado et al.[9] While in our process, we depend upon bandgap photons to drive the Ag into the As_2S_3, the spectral sensitivity of the photoresist system depends only upon the sensitivity of the evaporated AgBr. Figure 8 shows the optical absorption of our AgBr. We note that our sensitivity of about 1 mJ/cm^2 occurs in the region between 3500 and 4500 Å. In this wavelength region the absorption coefficient is of the order of 5×10^3 cm^{-1} for our Hg source. Therefore, a film

THE SURFACE - SENSITIZED PROCESS
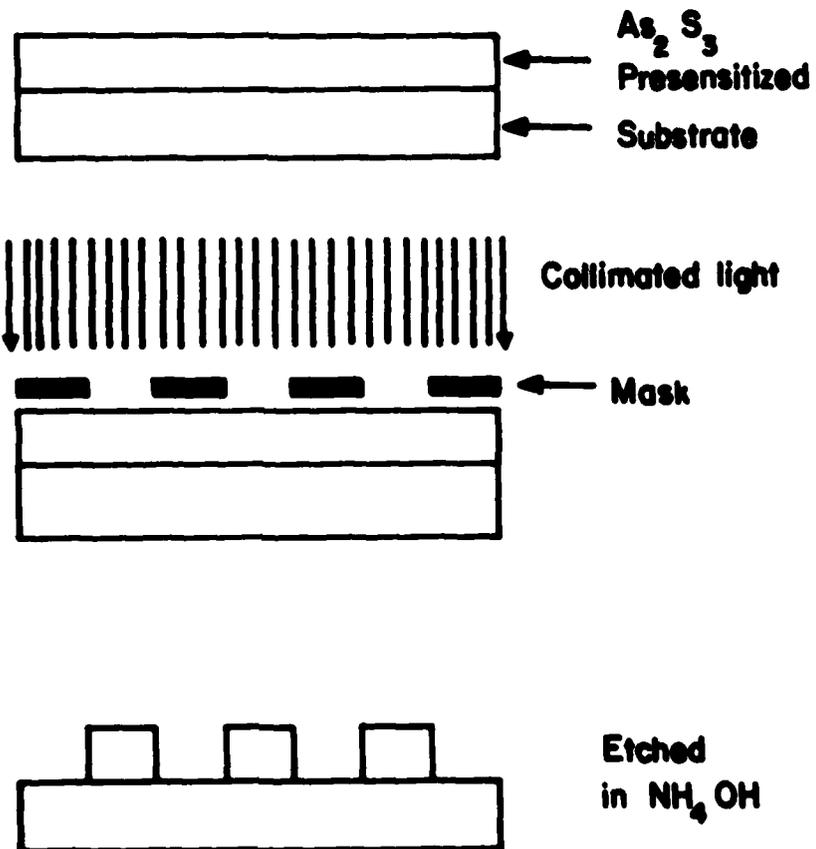
FIGURE 6

Block Diagram of the Surface-Sensitized Process

-16-
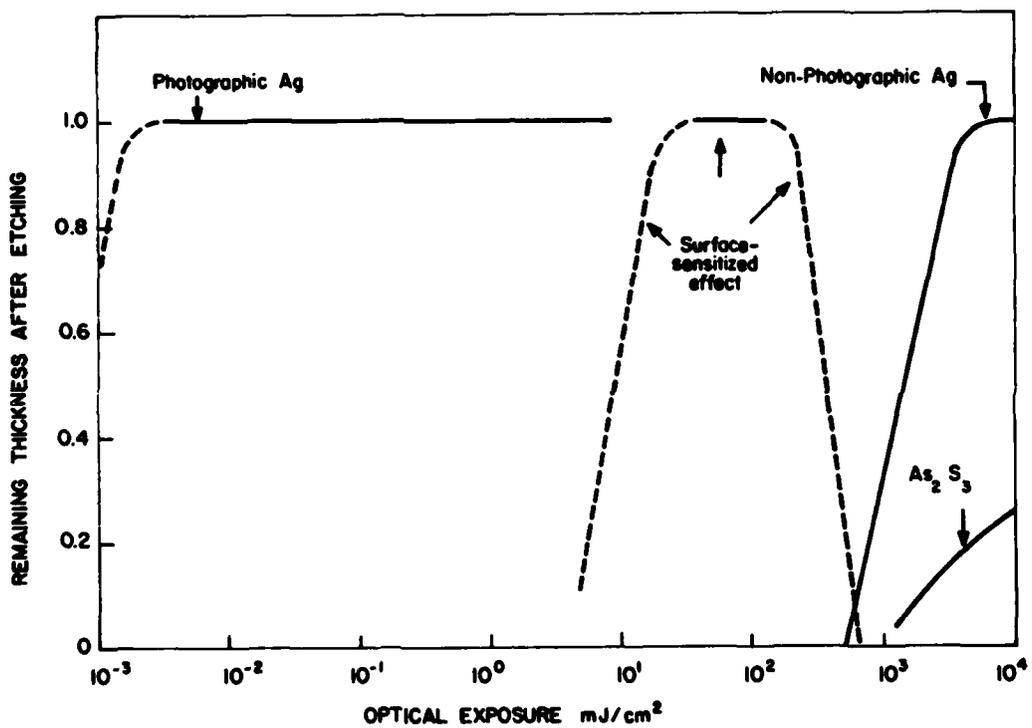
FIGURE 7

Optical Response of Several potential Inorganic Resists.

(This Figure compares the sensitivity of the Surface-Sensitized Process with metallic-Ag photodoping of As_2S_3 and with the positive imaging process (no metal) in As_2S_3.)

(Cp. Figure 3 for sensitivity of Ionomet Process)

For 2000Å thick film, sensitivity
measured at 2600Å was of the order
of 50 microJ/cm^2

FIGURE 8

Optical Absorption Spectra
of AgBr

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thickness in the vicinity of 2000 Å will absorb about 10% of the incident radiation. On the other hand, in the deep UV, where the absorption coefficient is of the order of 10^5 cm^{-1}, the same film thickness will absorb about 10 times more. We have tested the sensitivity of our films at 2600 Å and obtained well developed Ag images at $50\mu J/cm^2$.

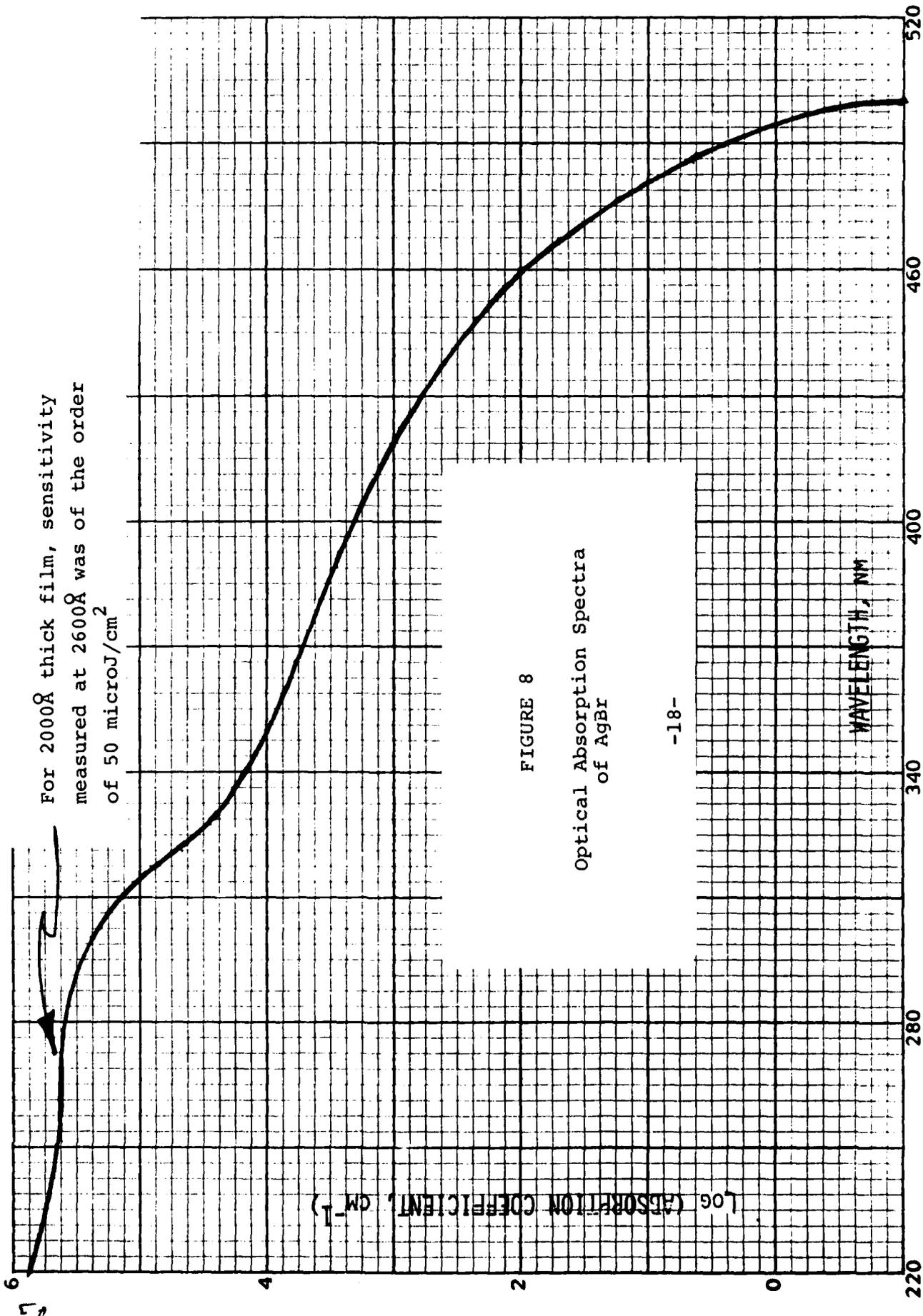Figure 9 shows the sensitivity of our films to electron-beam excitation. We see that even at a few keV we have a sensitivity of the order of $10^{-9} - 10^{-10}$ coulombs/cm^2. This sensitivity is too high to be useful for lithographic purposes since it implies about one electron/$(0.1\mu m)^2$ resolution element.

We have recently tested our films at the W x-ray wavelength of 7 Å. Figure 10 shows a plot of optical density as a function of incident energy density at 7 Å. We have obtained well developed Ag images at $5\mu J/cm^2$ at this wavelength.

D. Resolution

It is quite clear that photodoping of metallic Ag into As_2S_3 provides the resolution capability of the amorphous As_2S_3 with a relatively slow speed (1 J/cm^2). On the other hand, photodoping with an Ag image derived from an evaporated AgBr film provides a much higher speed ($5\mu J/cm^2 - 1$ mJ/cm^2 depending upon energy of incident photons) but is limited by the resolution potential of the AgBr. The surface-sensitized mode or photodoping with Ag derived from $AgNO_3$ has the resolution capability of the amorphous substrate with a speed intermediate between the other two processes (of the order of 50 mJ/cm^2). In these latter cases, the main draw-back, which results from the limited quantity of Ag deposited on the surface of the As_2S_3, is that the so-called capping or stability

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E-BEAM SENSITIVITY

E-BEAM SENSITIVITY OF OUR FILMS
MEASURED WITH 20KEV ELECTRONS CON-
FIRMED PREVIOUS MEASUREMENTS OF 10^{-9}
COULOMBS/CM^2. THIS SENSITIVITY TOO
FAST FOR LITHOGRAPHY. CORRESPONDS TO
ONE ELECTRON/ $(0.1 \mu)^2$

15KEV
7.5KEV
20KEV
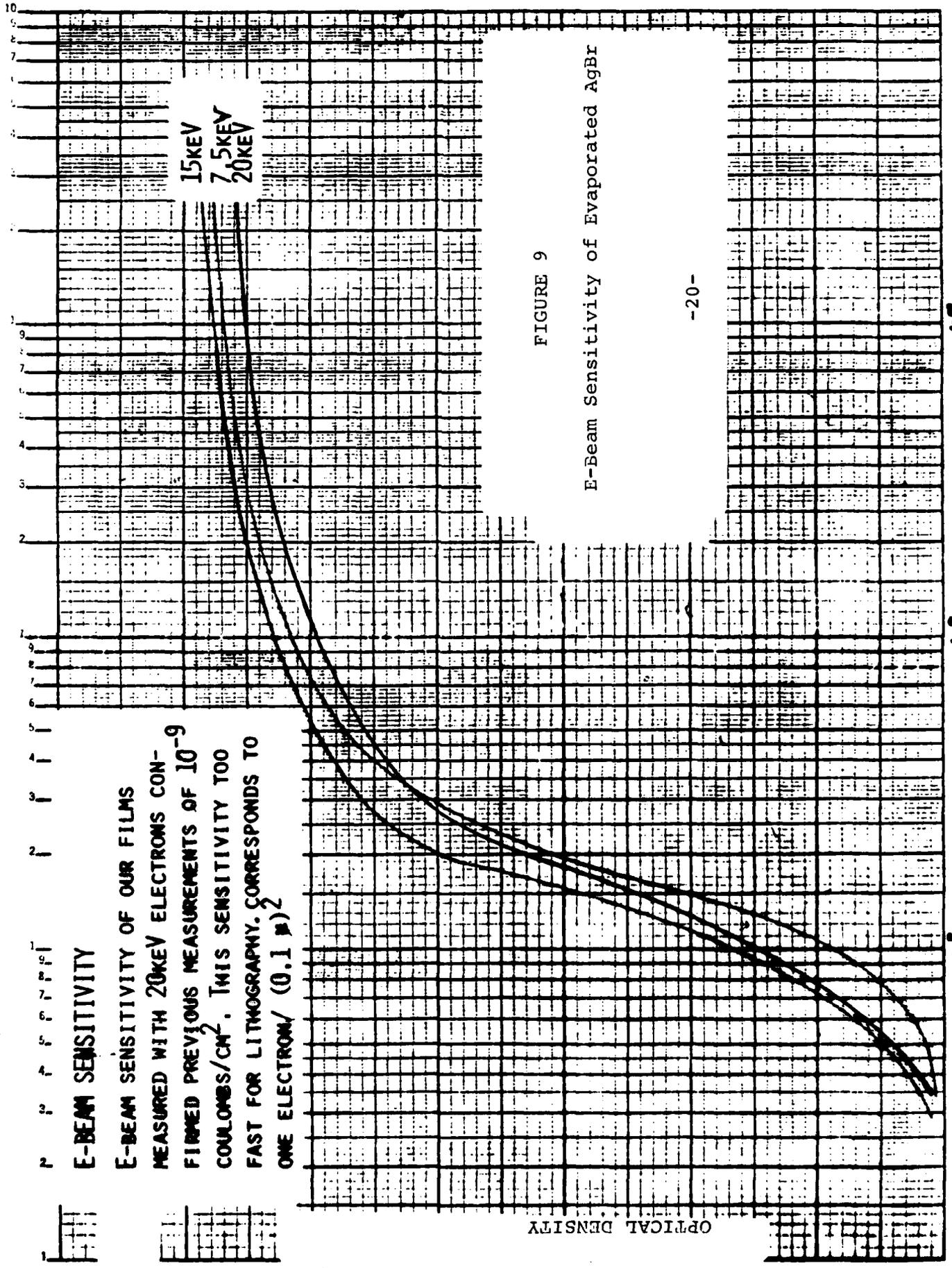
FIGURE 9

E-Beam Sensitivity of Evaporated AgBr

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OPTICAL DENSITY

EXPOSURE, ELECTRONS/CM^2

ENERGY DENSITY, microJ/cm^2

FIGURE 10

7Å X-Ray Sensitivity of Evaporated AgBr

to alkaline etching is not as great as in the case in which a large quantity of Ag is deposited on the surface.

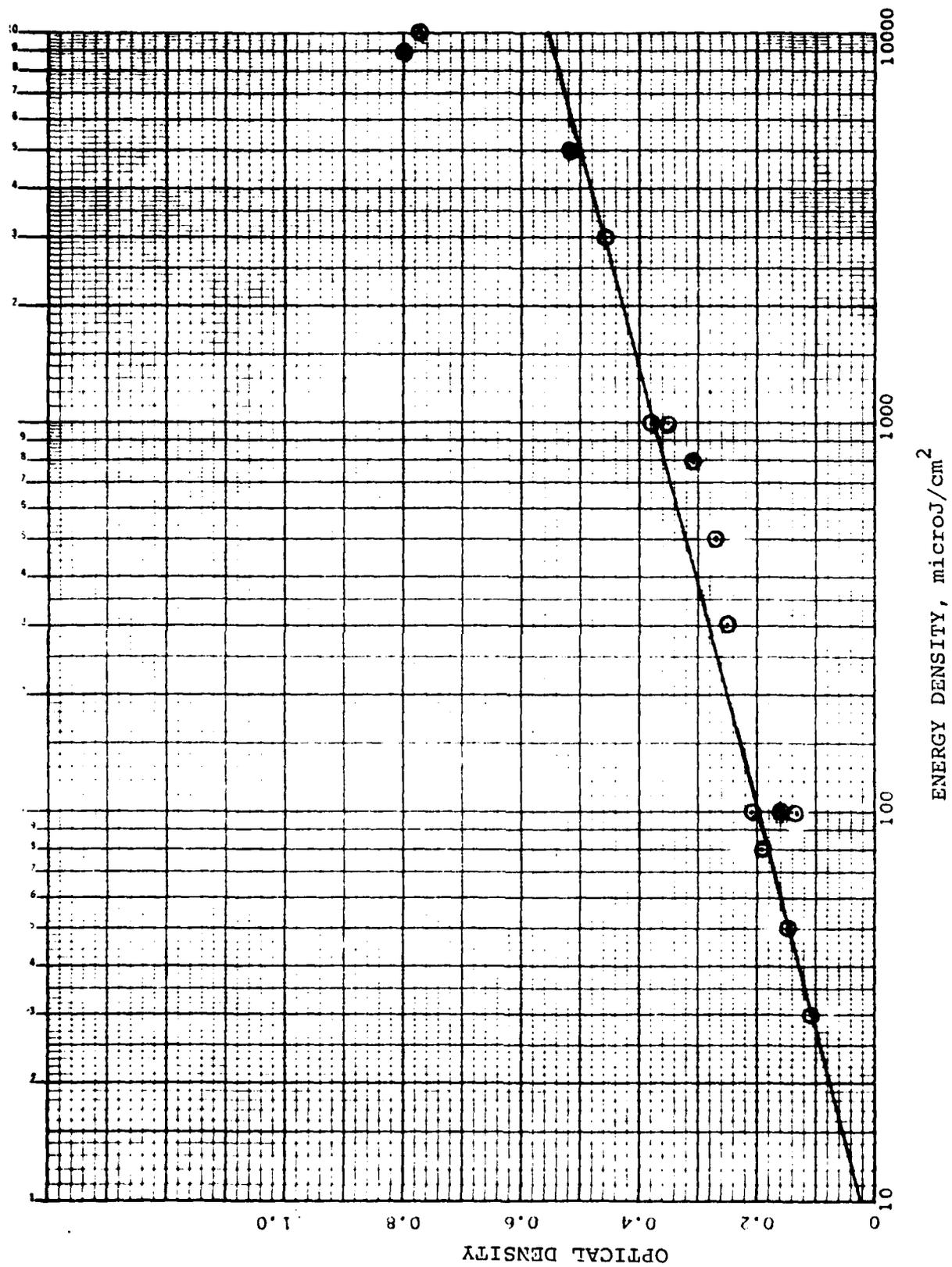One of our goals then was to examine our existing films and our development process and determine their resolution capability. A second goal was to assess those factors contributing to the resolution and assess the ultimate capability of this system.

Factors known to limit the resolution of evaporated AgBr layers include the size of the domains that make up the continuous layer and the spread of the image occurring during development. Our initial work, on films that were evolved principally for high sensitivity to positively charged ions, indicated that we had a grain size of the order of 0.15 microns. Our developer formulation, essentially a modified Mitchell[12] developer, promoted infectious development, which sometimes caused a whisker-like growth that extended over many contiguous domains. Such development techniques yielded high-speed and optically dense Ag images, were quite suitable for ion-beam mass spectroscopic use, but did not yield high-resolution imagery.

Toward the end of the first year, we undertook a program to decrease grain size and improve our development techniques. Our first effort to influence domain size was to increase the rate of deposition. Our second effort was to incorporate AgI into the melt. We added 3 molar percent which produced a decrease in average domain size of about 30%. Figure 11 shows histograms for undoped and iodide-doped AgBr films illustrating the improvement obtained. Our next direction was to cool the substrate during deposition. To this end we have designed and built a substrate cooler with liquid nitrogen feed which will enable us to cool over a range of temperatures. Recently, Assa[13] has reported on
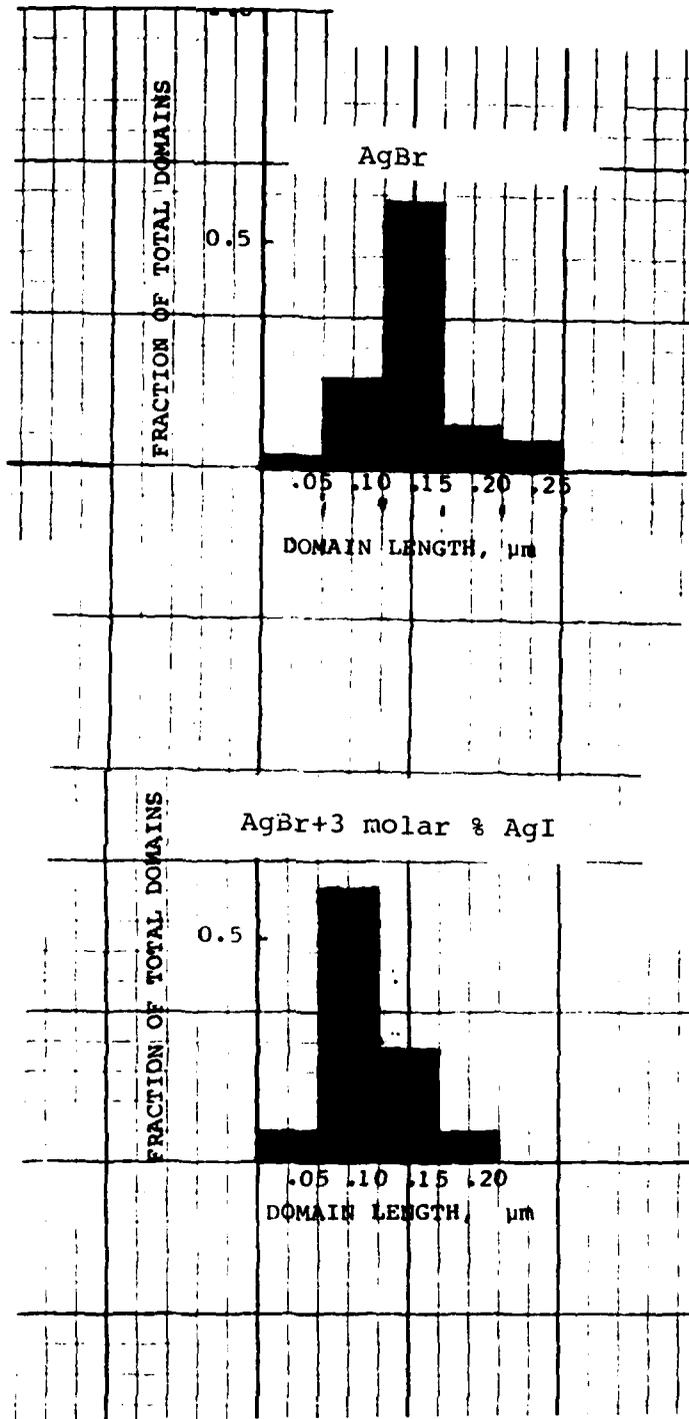
FIGURE 11

Histogram of Grain Size in AgBr
Compared with AgBrI

domain-size reduction with the inclusion of Rh into the AgBr films. The quantity of Rh is of the order of 0.25%.

Although the domain size remains the ultimate determinant for resolution, the development technique ranks just behind it in importance. We know, of course, that speed can be traded for resolution and both are dependent upon domain size and development technique. The Ag image obtained on development (modified Mitchell developer) of an x-ray exposed evaporated AgBr film is shown in Figure 12. The lacy appearance is characteristic of a whisker-like growth which extends over many domains. Our first effort to improve development involved decreasing the chemical development time and attempting to use a physical developer to provide additional silver. Chemical development is a process that makes use of the Ag present in the evaporated film. Physical development acts as an electroless plate and deposits Ag from Ag^+ contained in the developer solution. The modified Mitchell developer, employed with evaporated AgBr for many years, consists of a mixture of gelatin, $Na_2S_2O_3$, Na_2SO_3, hydroquinone, Elon, and two carbonates to control the pH of the aqueous system. The thiosulfate ($Na_2S_2O_3$) etches the AgBr and complexes the Ag^+ released so that it is unavailable for deposition on latent image sites. It plays an important role in that it attacks domain boundaries and tends to isolate each domain as an individual grain. Silver ions from the unexposed portions of the film enter the aqueous solution and are then reduced by the hydroquinone and Elon. It has been known that, in the case of emulsions, Elon produces a finer grain development than hydroquinone. In the case of evaporated AgBr deposited on As_2S_3, we have observed exactly the opposite, namely hydroquinone provides finer grains with no whisker growth and Elon
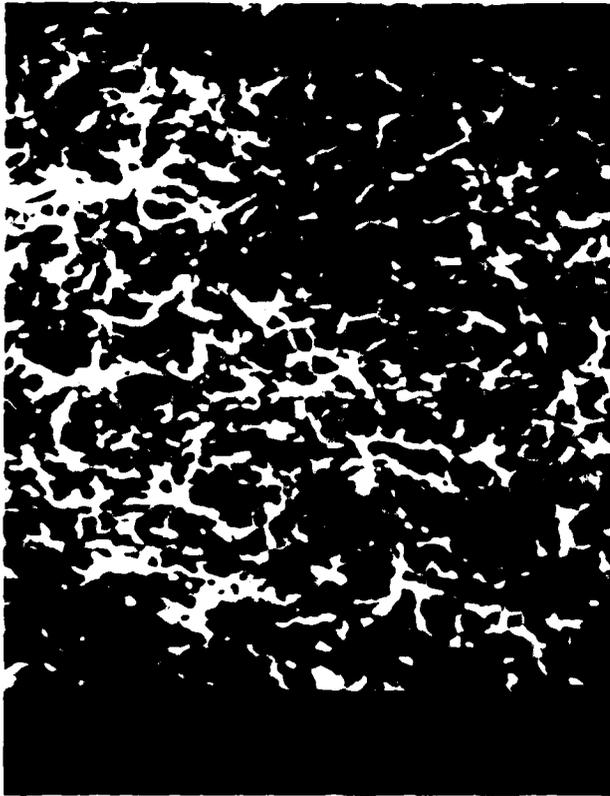
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FIGURE 12

Electron Micrograph of X-Ray Exposed and Mitchell Developed
Ag Image. 10kx.

promotes whisker growth. Our effort in developing a process for fine-line lithography has been to slow down the development rate to prevent whisker growth, to ensure that sufficient thiosulfate was present to separate grains, and to formulate a physical developer that would increase the gamma of our system.

III. RESULTS

During this first year we have:

1. Evaporated amorphous As_2S_3 and generated positive relief images using bandgap radiation.

2. Performed Ag photodoping of As_2S_3 using evaporated Ag films ranging in thickness from 0 Å to 1000 Å and generated negative relief images.

3. Performed Ag photodoping of As_2S_3 using Ag derived from aqueous solutions of $AgNO_3$, and generated negative relief images.

4. Developed a technique for Ag photodoping of As_2S_3 using evaporated films of AgBr to provide a very thin layer of Ag and generated negative relief images.

5. Showed that our concept of Ag photodoping using photographic Ag derived from evaporated AgBr was viable, provided very high speeds, and generated negative relief images.

6. Showed that evaporated AgBr films could provide photographic negative relief images in the deep UV with energy density of the order of $50 \mu J/cm^2$.

7. Showed that evaporated AgBr could provide sensitivities to 20 keV electrons of the order of $10^{-9} - 10^{-10}$ coulombs/cm^2.

8. Showed that evaporated AgBr could generate negative relief images with 7 Å W x-ray exposures of the order of $10\mu J/cm^2$.

9. Improved the resolution capability of evaporated AgBr on As_2S_3 from $3\mu m$ to approximately $.5\mu m$.

Using evaporated Ag films ranging in thickness from 30 to 1000 Å we have been able to obtain negative relief images in As_2S_3 films approximately 3000 Å thick. Figure 13 shows a photograph of a sample in which a 100 Å layer of Ag was photodoped into As_2S_3 with approximately 0.85 J/cm^2. The surface was then etched in an Ag etchant and the As_2S_3 was etched in NH_4OH. Such systems have potentially good resolution, suffer from difficulty in removing the Ag in the unwanted regions, have essentially no shelf-life between Ag deposition and exposure, and are extremely slow.

Figure 14 shows two photographs, one at 50x and one at 200x, of a surface-sensitized relief image. This sample was coated with a film of evaporated AgBr which was then treated in such a way as to deposit an extremely thin layer of Ag. The sample was exposed with 40 mJ/cm^2 and etched for 15 seconds in 28% NH_4OH. This system has the advantage of reasonably higher speed (contrasted to metallic-Ag photodoping) and with excellent resolution, limited only by the nature of the amorphous substrate, but it suffers in its capping from a limited quantity of Ag. However, if we reduce the thickness of the As_2S_3 we may then achieve similar speed with better stability in the etching environment.

The resolution capability of our films at the outset of this program was of the order of $3\mu m$. The infectious development that we described is illustrated in Figure 15. In this photograph we show a sample exposed on a GCA Mann DSW 4800 Step-and-Repeat Exposure
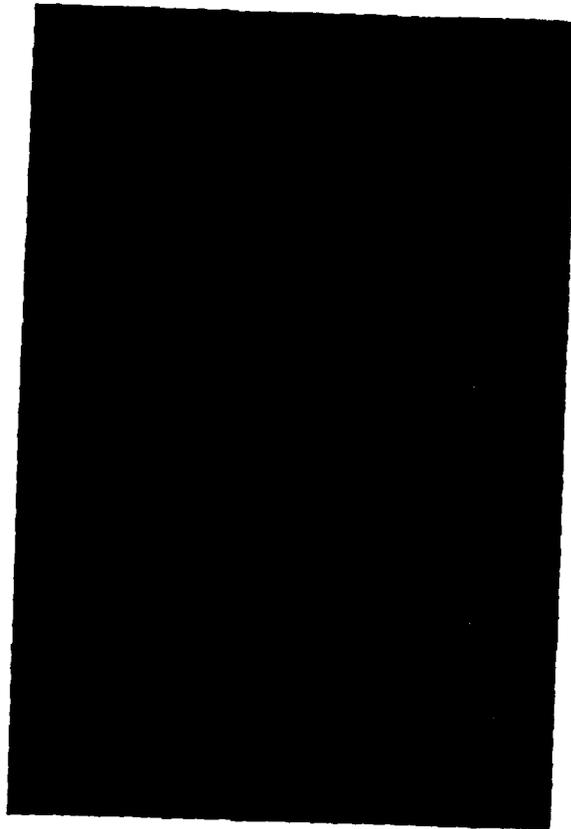
FIGURE 13

Photograph of Metallic-Ag Photodoped As_2S_3 Sample.
(Low-resolution contact print. Evaporated Ag, 100Å
thick, photodoped for 5 mins at 2mwatts/cm^2, etched
in NH_4OH. Resolution of this process as good as
the optical system.)

50x

200x

FIGURE 14

Two Photographs of Surface-Sensitized Relief Images (50x and 200x).

(Evaporated AgBr layer treated to yield thin Ag coverage,
  exposed for 15 secs at 2mwatts/cm^2, etched for 15 secs in
NH_4OH. Dark regions are As_2S_3, bottom lighted.)

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FIGURE 15

Photograph of Evaporated AgBr Image on As_2S_3 Exposed on GCA
Mann DSW 4800.

(Numbers alongside the resolution
pattern are in microns.)

System. The quality of films used at the outset of this program is clearly seen. In Figure 16 we show a contact print of a sample of AgBrI, where 1.25μm lines are clearly resolved. It is extremely difficult to obtain submicron exposures by conventional techniques. In order to assess the capability of our films we have resorted to the use of near-field diffraction patterns. Figure 17 shows a sample of AgBrI deposited on As_2S_3 and contact exposed with a mask containing 4 each 1.25μm lines and 3 each 1.25μm spaces. Near-field diffraction can produce in this 8.75μm space 12 lines, each line being 1/23 x 8.75μm, or roughly 1/3 of a micron.

IV. CONCLUSIONS

On the basis of this first year's work we believe that the combination of the chalcogenides (in particular, As_2S_3) and evaporated AgBr offer tremendous research potential in the field of microlithography. In this period we have shown that evaporated AgBr has extremely broad spectral capability with sensitivity ranging from the UV to the deep UV, to x-ray, to e-beam, and even to ion-beam sources. The sensitivity over this entire spectrum exceeds that of any other known material by virtue of the amplification provided by the development process. We know that all existing polymer resists offer essentially one event/photon. Only the AgH system, of all known photographic systems, offers a multiplication in the development process. This multiplication or gain can be controlled and may range as high as 10^8. (In our high-resolution samples we have measured gains of 10^5.) This gain, of course, comes about at the expense of resolution. We have already shown in the brief period during which we have tackled the problem, that significant improvements in resolution can be made without

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FIGURE 16
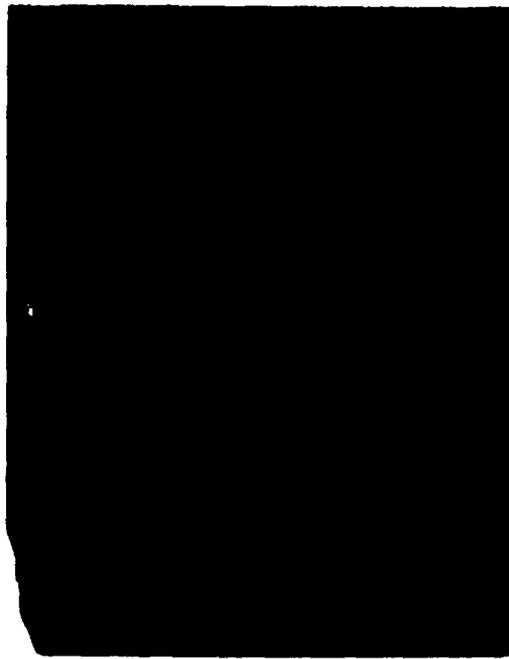
Photograph of As_2S_3 with 1.25 Micron Lines Cleanly Resolved.
Evaporated Layer Contains Mixture of AgBr and AgI. Modified
Mitchell Developer. (Optical contrast of photograph limited
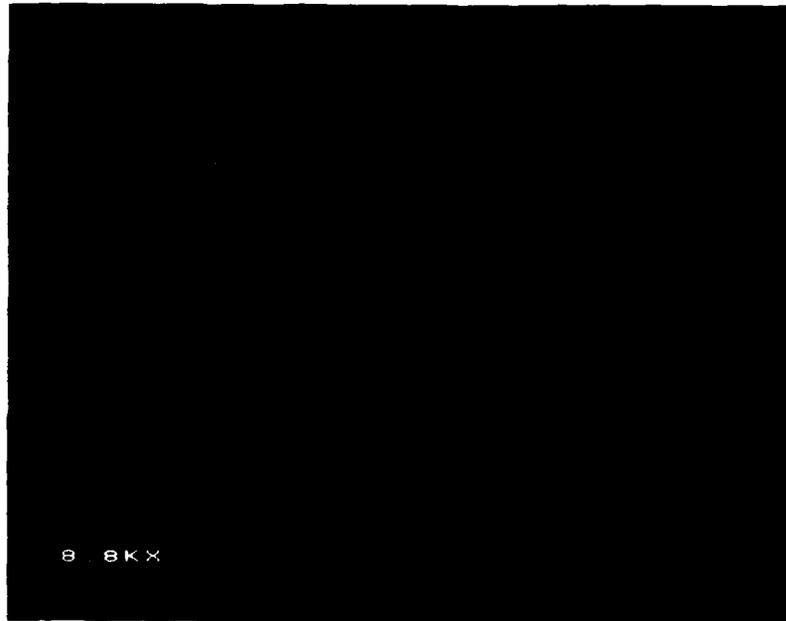by optical system used to photograph the lines.)

FIGURE 17

Submicron Lines on As_2S_3 Using AgBrI and State-of-the-Art
Developer. Exposure by Near-Field Diffraction (therefore lines
are not clean) (8.8kx)

degrading speed. This means that we are nowhere near the (speed) x (resolution) limit of our evaporated AgBr films. We believe that domain size can be reduced below 0.1μm and that development techniques will enable us positively to achieve, in the near future, 0.5μm line capability. A potential for 0.5μm lithography with the tremendous speed advantage of AgBr to all radiations currently being investigated for application to submicron patterning can hardly be ignored. For example, to achieve enhanced absorption for x-ray lithography a large effort[14] is under way to incorporate Cl or Br into organic polymer resists. We already have an absorption to x-rays of the order of 30% with our 2000 Å films. Furthermore, the development process enhances our speed even more. Figure 18 shows a contact print of evaporated AgBr taken at 7 Å with approximately $10\mu J/cm^2$.

Such a speed advantage can have significant impact upon x-ray lithography. For example, to achieve exposures that require only a few minutes necessitates brute forcing the x-ray source.[15] The size of the target area and the distance of source to sample must be compromised to permit exposures even in this time scale. Both of these degrade the image because of the penumbral effect due to spacing of the mask from the sample by several tens of microns. During such long exposures, heating and vibration can further degrade the imagery. Finally, any improvement in speed increases throughput which is not to be ignored.

The next major thrust in lithography may very well occur by retrofitting existing step-and-repeat-on-the-wafer cameras to deep UV. A decrease in wavelength by a factor of two could bring production capability into the submicron region. We are seeing much
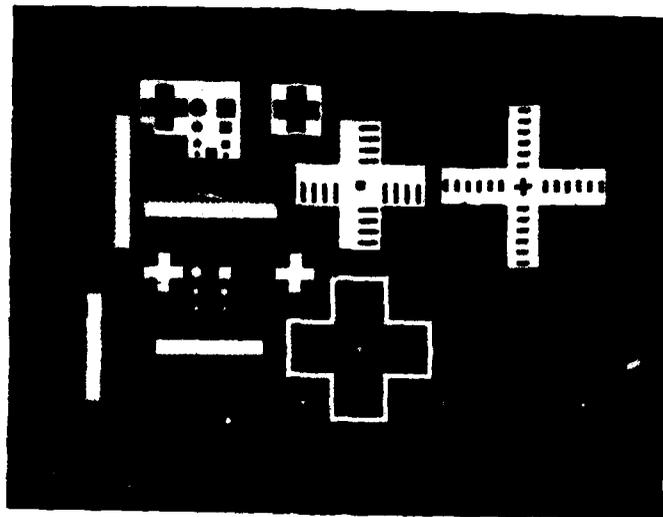
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FIGURE 18

Photograph of a Ag Image Obtained by Contact Printing with
W X-Rays (7Å).

effort in the development of polymeric deep UV resists.[16,17]
However, none of the polymer type resists has any significant
speed at these wavelengths. A fast resist, with submicron reso-
lution capability, could catalyze effort in this area. We are
suggesting that evaporated AgBr can provide adequate resolution
which will more than match the resolution capability of deep UV
exposure systems.

The exhibited high sensitivity of our evaporated films to e-
beams need not preclude its use in this area of lithography.
Although we have not addressed the problem there is much that can
be done. For example, we can incorporate ions into the lattice
that provide a substantial decrease in sensitivity. We can reduce
the thickness of our films to reduce the effective absorption.
We can alter our development procedures so that there is a smaller
build-up of Ag on each latent image site. We can decrease domain
size even further and by so doing increase resolution at the ex-
pense of speed provided that we have attained the full (speed) x
(resolution) product of our films. Finally, if the beam power
can be significantly decreased, this would go a long way toward
making AgBr a feasible e-beam resist. As noted in Figure 9, films
of the order of a few thousand Angstroms thick have virtually the
same sensitivity at 7 keV as at 20 keV. This sensitivity extends
down to 5 keV.[18] The need for high voltage comes about from the
beam dynamics required with a high-current density beam. The need
for high current density stems, of course, from the insensitivity
of existing polymer resists. Therefore, if the beam power were
reduced, then present AgBr layers might be a viable candidate for
e-beam lithography.

It is also very interesting to speculate upon the possibility of using domain-size control to effect control over speed where high resolution is not required. For example, it is now proposed to use combinations of optical and e-beam exposure on different layers of a device structure in order to obtain the speed of the optical system and the resolution of the e-beam system. Suppose we could easily generate a large domain AgBr film for those layers with low resolution. Then even for low-resolution work the speed of the e-beam system might not prove disadvantageous. Extending this speculation further, since we know that domain sizes can be increased by annealing at reasonable temperatures, can we conceive of a pre-electron exposure system consisting of a computer-controlled long-wavelength laser which annealed each AgBr film in such a manner that the appropriate areas of the film had large domains and the rest had small domains. Such a system could then accommo-date to all image sizes.

Ion-beam writing has been noted as a potential technique for submicron lithography.[19] Some work has been done in this area, but not nearly as much if a suitable ion-beam sensitive resist were available. At present the only commercial use of evaporated AgBr is as a photographic material for ion beam recording. Ionomet's evaporated AgBr films have, for the past 10 years, been sold as ion-beam mass spectrometer plates. For high mass numbers, there is nothing able to provide equal sensitivity. Therefore, in yet another imminent lithographic area, evaporated AgBr films have very important potential.

As we have shown, the photographic Ag image generated from evaporated AgBr at any suitable wavelength may be photodoped into

As_2S_3 with bandgap photons. In a similar manner, this may be done with other chalcogenides or with any other material exhibiting the property of photodoping. However, in the case of the chalcogenides, and as best known to us, As_2S_3, it is possible to photodope using metallic Ag layers a few Angstroms thick generated in any of several different ways. Such procedures are slower than AgH, but offer unlimited resolution capability. They also offer the possibility of changing and possibly controlling the gamma of the resist and thus matching or tuning the resist to the optical system.

A few Angstroms of Ag or evaporated AgBr deposited on a very thin layer of As_2S_3 on top of a polymer on top of Si, or an evaporated AgBr film on top of a polymer on top of Si offer very exciting microlithographic possibilities.

During the second year of this program we should like to be able to address all of the problems mentioned but we recognize that the magnitude of the effort and the time allotted will preclude such an undertaking. We therefore have proposed to examine the factors contributing to the resolution of the evaporated AgBr films, namely to study these factors, to reduce the size of our domains, and to undertake a restructuring of our development process. We will also perform work on the chalcogenide As_2S_3 but the effort here will play a secondary role.

V. REFERENCES

1. M.R. Tubbs and A.J. Forty, Brit. J. Appl. Phys. _15_, 1533 (1964).

2. M.T. Kostyshin, E.V. Mikhailovskaya, and P.F. Romanenko, Soviet Phys. Solid State _8_, 451 (1966).

3. H. Sakume, I. Shimizu, H. Kokado, and E. Inoue, Proc. 3rd Conf. Sol. St. Devices, Tokyo, 1971.

4. T. Shirakawa, I. Shimizu, H. Kokado, and E. Inoue, Phot. Sci. Eng. _19_, 139 (1975).

5. H. Nagai, A. Yoshikawa, Y. Toyoshima, O. Ochi, and Y. Mizushima, Appl. Phys. Lett. _28_, 145 (1976).

6. K.D. Kolwicz and M.S. Chang, J. Electrochem. Soc. _127_, 135 (1980).

7. J.I. Masters, G.M. Goldberg, and J.M. Lavine, IEEE _EDL-1_, 61 (1980).

8. _D. Goldschmidt and P.S. Rudman, J. Non-Cryst. Sol. 22, 229 (1976)._

9. H. Kokado, I. Shimizu, and E. Inoue, J. Non-Cryst. Sol. _20_, 131 (1976).

10. J. Malinowski and A. Buroff, Contemp. Phys. _19_, 99 (1978).

11. A. Buroff, E. Nebauer, P. Sputitz, and I. Willert, Phys. Stat. Sol. (a) _40_, K195 (1977).

12. A. Yoshikawa, O. Ochi, H. Nagai, and Y. Mizushima, Appl. Phys. Lett. _29_, 677 (1976).

13. A. Buroff, P. Simidchieva, K. Kolev, and R. Stoycheva, Proc. Intl. Conf. Phot. Sci., Rochester, NY, August 1978, p. 243.

14. G.N. Taylor, Sol. St. Tech. _23_, 73 (1980).

15. W.D. Buckley and G.P. Hughes, Ext. Abst. Electrochem. Soc. _80-1_, Abs. #276, p. 699 (1980).

16. C.W. Wilkins, Jr., E. Reichmanis, and E.A. Chandross, J. Electrochem. Soc. _127_, 2510 (1980).

17. E. Reichmanis, C.W. Wilkins, Jr., and E.A. Chandross, J. Electrochem. Soc. 127, 2514 (1980).

18. A. Shepp, R.E. Whitney, and J.I. Masters, Phot. Sci. Eng. 11, 322 (1967).

19. R.L. Seliger, R.L. Kubena, R.D. Olney, J.W. Ward, and V. Wang, J. Vac. Sci. Tech. 16, 1610 (1979).

IV. LIST OF PUBLICATIONS

1. G.M. Goldberg, J.M. Lavine, J.I. Masters, P.A. Thompson and Z.Y. Vayman, IEEE IEDM, Washington, DC, December 1979, Abstract #3.7, p. 62.

2. J.I. Masters, G.M. Goldberg and J.M. Lavine, IEEE EDL-1, 61, (1980).

3. J.M. Lavine, J.I. Masters and A. Das, IEEE IEDM Washington, DC, December 1980, paper no. 16.6.

4. J.M. Lavine, J.I. Masters and A. Das, "A Multilayer Photoresist System for Submicron Imaging Employing Evaporated AgBr as the Photosensitive Layer for Deep UV, E-beam and X-ray Lithography", 2nd International Symposium on Model Investigations of the Photographic Process and New Photoregistering Systems, Drouzhba, Bulgaria, September 1980.

5. J.M. Lavine, J.I. Masters, D.E. Bailin, Z.Y. Vayman and A. Das, "A Two-Layer Photoresist System Employing Evaporated AgBr" to be submitted to J. Electrochem. Soc.

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