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THE ABILITY OF SURFACTANTS TO ASSIST IN THE REMOVAL OF IMAGE SCUM IN POSITIVE RESIST DEVELOPMENT

by

Michael P. Belden

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in the School of Photographic Arts and Sciences in the College of Graphic Arts and Photography of the Rochester Institute of Technology

May, 1982

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COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY

THE ABILITY OF SURFACTANTS TO
ASSIST IN THE REMOVAL OF IMAGE SCUM
IN POSITIVE RESIST DEVELOPMENT

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Submitted to the
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ABSTRACT

An experiment was run to determine the ability of surfactants to reduce or remove scum produced during development of a positive resist. Anionic, cationic and nonionic surfactants were added to a low metal ion developer at concentrations between 0.025% and 0.5%. The film thickness loss due to development was measured, and image profiles were observed with scanning electron micrographs. Of the surfactants tried, Aerasol OT-75 (dioctyl ester of sodium sulfosuccinic acid) produced the best results, 9.5% film thickness loss with little image profile change. However, the experiment was limited by processing condition variables.

ACKNOWLEDMENTS

The author would like to thank a number of people who assisted in the completion of this paper

Dave (Lefty) Jansen, who was instrumental in the modification of the GCA spinner. Without his help this work never could have been completed.

For the production of the scanning electron micrographs, I have three people to thank. John Johnson, for his time and effort with the SEM at RIT. Robert Zawierucha, Manager of the Materials Engineering Labratory at Union Carbide, for the use of their SEM. To Dan Kmiotek, Senior Technician of the SEM, for his actual time and work on the final images.

For their help in getting materials and equipment, Marshall Yost and John Guild of the Eastman Kodak Company.

And finally, my advisor Frederick Rauner and the Eastman Kodak Company for the support they have given me on this project.

DEDICATION

This thesis is dedicated to

my parents, Joan and Bob,

who have generously helped me

through my career at RIT,

my loving thanks.

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INTRODUCTION

The use of sophisticated methods for the aquisition and processing of large amounts of information has created a need for developing very high density electronic circuits. These circuits, called "chips", are becoming more and more common in everyday life. Home computers, calculators, video games and many other common devices make use of integrated circuits.

The fabrication of these chips utilizes Ultra Violet (U.V.) radiation sensitive materials called photoresists. These materials change their structure upon exposure to U.V. radiation. This change in structure is accompanied by a change in solubility of the photoresist in an appropriate solvent. There are two types of photoresist materials, negative photoresists and positive photoresists.

Negative photoresists can be characterized by a photopolymerization or photocrosslinking process. For example, the development of a photocrosslinkable polymer is based on the principle of photodimerization of cinnamic acid or its esters. When the polymer is exposed to U.V. radiation there is an increase in molecular weight. This increase in molecular weight is accompanied by a decrease in solubility of the resist in a solvent.[1] An example of a negative resist

that utilizes photocrosslinking is Kodak Photo Resist Polyvinyl Cinnamate.[2] The negative process is diagramed in Figure 1a.

Positive resists, unlike negative resists, are degraded by exposure to U.V. radiation. This photomodification results in an increase in solubility of the resist in its developer, an alkaline solution.[4] The U.V. radiation transforms the photoactive compound (substituted o-napthoquinonediazides, diazo-oxides) into an alkaline soluble material. This material is believed to be an indenecarboxylic acid formed from an intermediate ketene generated by the U.V. radiation.[5] In the presence of water the ketene reacts with the water to form a 3-indenecarboxylic acid. Without the presence of water, an ester is formed instead of an acid, and this can produce a crosslinking effect. (See Figure 2). The positive process is diagramed in Figure 1b.

The desire to continually shrink the dimensions of semiconductor-integrated circuits has caused a growing interest in positive photoresists over the past several years. This is due to a number of advantages of positive systems, specifically, their inherent high resolution,[6] their ability to resist swelling, their ability to allow thicker coatings and still provide good step coverage with lower pinhole density.[7]

There are also some limitations to positive systems,

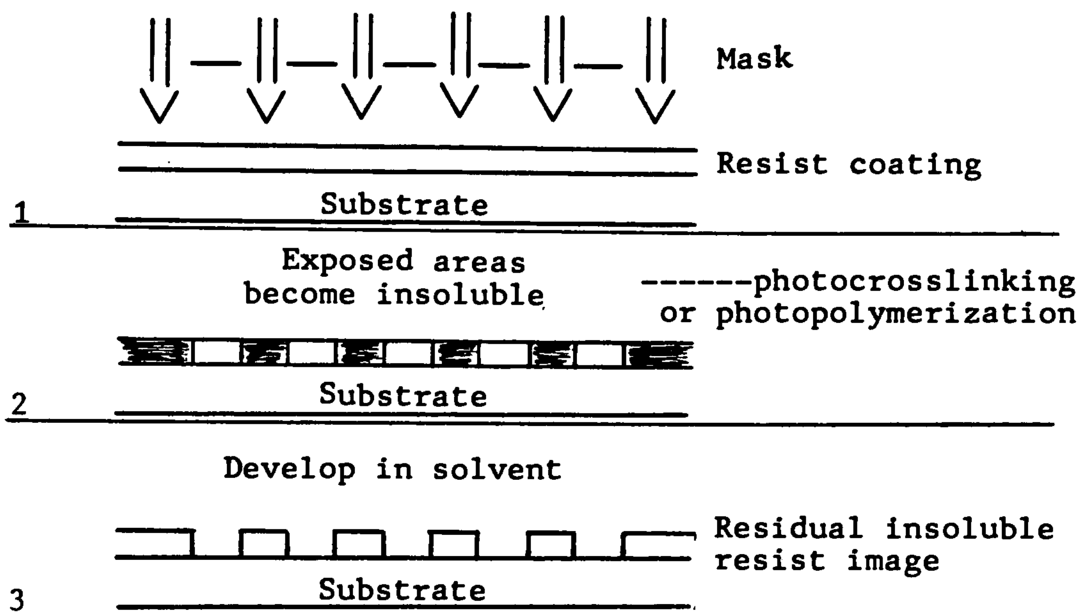

Figure 1a. Negative working systems.

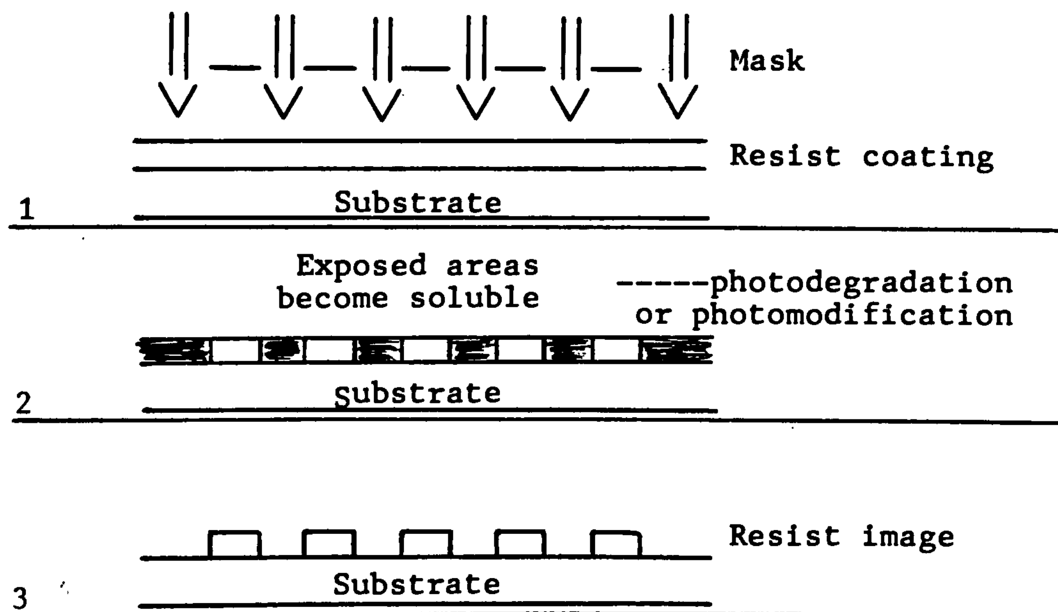

Figure 1b. Positive working systems.

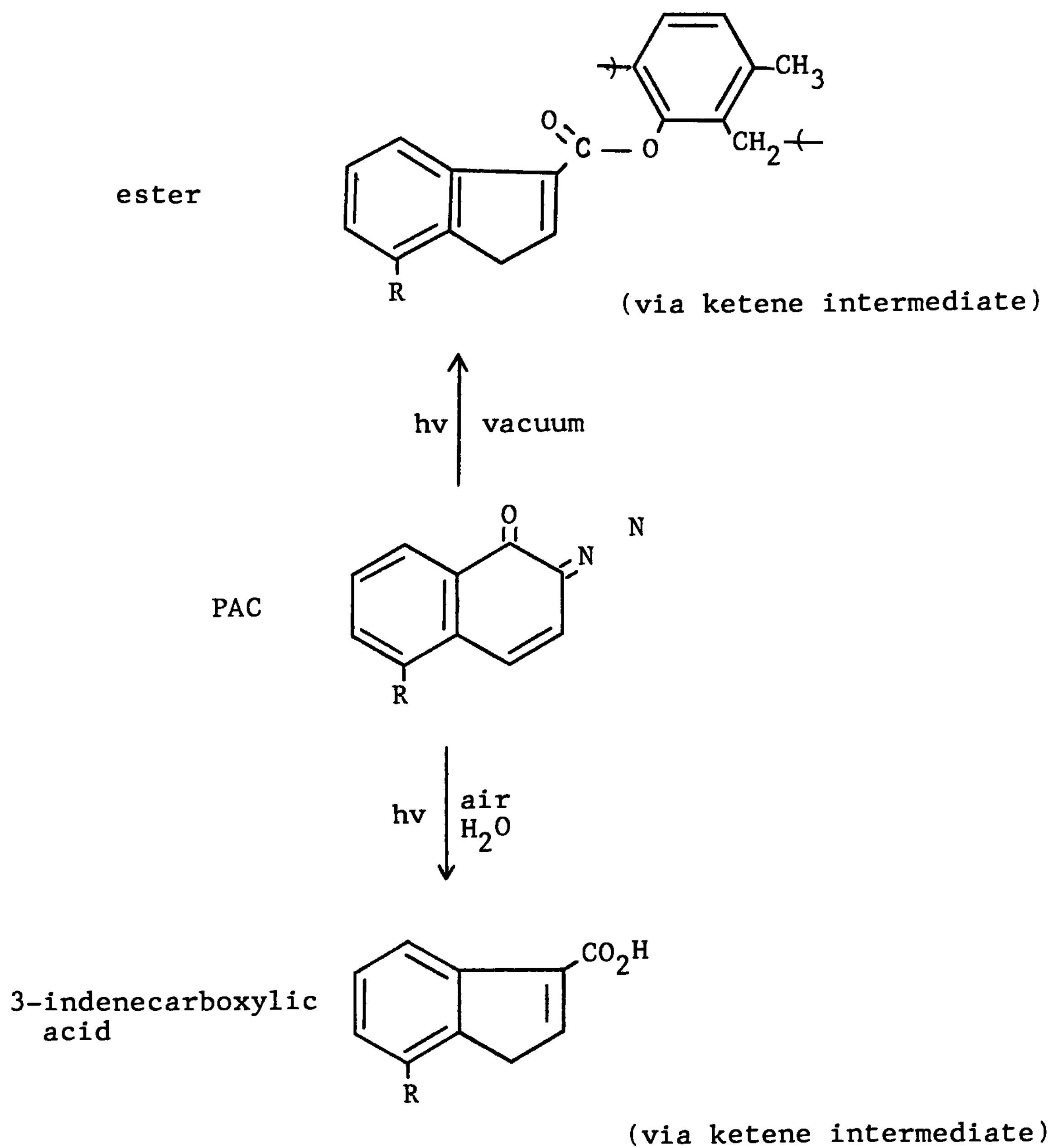

Figure 2. U.V.-induced decomposition pathways for the photo-active compound (PAC).

though. Some of these are lack of repeatability,[8] bottle-to-bottle variations,[9] slower photospeed and therefore lower throughput and higher processing costs.[10] But even with these limitations the trend is to switch to positive resists due to their high resolution and excellent step coverage.

A problem that can be encountered with either positive or negative photoresists is that image scumming (incomplete development) can occur. This scum limits resolution and is undesirable.

Deforest[11] suggests that there are four basic causes of this scumming:

1. Incompletely removed photoresist
2. Resist constituents that are precipitated from the developing solution
3. Resist constituents that bleed out during and after development
4. Films that are formed by non-resist-related contaminants precipitated from the developer.

Underdevelopment or depleted developer will cause an excessive amount of resist to remain in the nonimage areas. The second type of scum is caused by anything that reduces the solubility of removed resist constituents. One of the major causes of this is incorrect dilution of the developer. Overdevelopment will cause the third type of scum. The fourth type of scum is the rarest. This occurs when the developer comes into contact with other plastics. This

incomplete development occurs either by reducing the resist solubility, or by precipitating on its own; which actually occurs is not known.[12]

Another method to reduce or eliminate scumming is described by Flowers and Smith.[13] They used a photoresist overcoat consisting of a surfactant, lubricant and a free radical inhibitor in solvent. The surfactant and the lubricant were used to reduce the photomask-photoresist interactions which decreases defect densities. The free radical inhibitor absorbed and stray light energy that may have gotten under opaque mask areas. They found that this imlproved fine-line resolution and reduced scum film formation. This technique involves the addition of another step into the process.

Plasma descumming is used to eliminate scumming problems. This process uses an oxygen plasma to oxidize the remaining scum to CO_2 and water. The plasma would also have an effect on the image areas but it is not significant.

Using surfactants in the positive resist developer in order to reduce or remove scum has been suggested. Surfactants ate typically long hydrocarbon chains that have a hydrophobic characteristic on one end of the chain and a hydrophilic (polar) group attached to the other end.[14] There are three types of surfactants, anionic, cationic, and nonionic. They differ by the type of polar group that is attached to the hydrocarbon chain.

A consequence of adding a surfactant to the developer is that it can cause removal of more than just the scum. The overall film thickness can be reduced. Normal development causes a decrease in overall film thickness, but the addition of a surfactant can cause this loss to increase, due to the surfactant acting as a resist solvent and/or significantly improving the wetting characteristics of the developer. The film thickness loss should be kept to a minimum in order to keep the pinhole density low and to assure complete step coverage. It is therefore important to try to pick a surfactant that will minimize this film thickness loss.

EXPERIMENTAL

1. Materials:

A. Substrate and Resist-

Kodak Micro Positive Resist 809 was diluted 5:1 with Kodak Micro Positive Resist Thinner 809. The resist was spin coated at 3500 RPM onto 2.5 $inch^2$ chrome-clad glass plates using a modified GCA inline coater/developer/source dispenser. The Eastman Kodak Company supplied both the resist and the chrome-clad glass plates.

B. Surfactants-

The surfactants that were used represent the three major categories of surfactants: anionic, cationic, and non-ionic. The choice of surfactants was made on the basis of their availability. The nonionic surfactant was Triton X-100, an octylphenoxy polyethoxy ethanol, obtained from the Rohm and Haas company. Four anionic surfactants were tried, three of them were from the Niacet Corporation and the fourth was from the American Cyanamid Corporation. The Niacet Corp. products were Niaproof 4 (sodium tetradecyl sulfate), Niaproof 7 (sodium heptadecyl sulfate), and Niaproof 08 (sodium 2-ethylhexly sulfate). The American Cyanamid Corp. product was Aerasol OT-75 (dioctyl ester of sodium sulfosuccinic acid), and the cationic, Hyanine 1622 (quaternary ammonium salt),

was also aquired from the Rohm and Haas company.

C. Developer-

Kodak Low Metal Ion Developer 809 diluted 1:13 with distilled water was used. The three surfactants were added at various concentrations ranging from 0.025% to 0.5%. Kodak's processing recommendations were used as a starting point.

2. Apparatus:

A. Spinner-

A GCA inline spinner was modified so that it could be used in a non-inline manner. Spin speed was controled by connecting a potentiometer to the power supply. The spin speed was determined using a strobe light calibrated with a voltmeter connected to the potentiometer. A separate vacuum pump was used to provide the necessary vacuum pressure to keep the plates on the chuck.

B. Exposing Device-

A Colight Inc. Atlantic Printer with a vacuum back was used to expose the coated plates. This is a diazo printer with a high pressure mercury vapor lamp which is a source recommended for exposing 809 resist.[16] However the printer uses a glass plane for creating the vacuum and this is not suitable for obtaining good quality images. The two glass interfaces with the mask introduce considerable standing wave effects.

C. Oven-

A precision Scientific Thelco Model 18 forced air oven was used to prebake the resist.

D. Film Thickness Measuring-

A Sloan Dektak stylus-type film thickness measuring device was used to determine the film thickness before and after development. This device tracks a stylus across the surface of the resist image and prints out changes in thickness as compared to a baseline measurement.

3. Processing:

The thinned resist was applied to the surface of the chrome-clad glass plate and spun for 30 seconds at a spin speed of approximately 3500 RPM's. This produced a uniform film thickness of approximately 1μm. The resist was then prebaked for 30 minutes at 90°C. A 13-second exposure was used to produce the images. Dip-and-dunk processing for 40 seconds at 21°C was used to develop the plates. A piece of Estar based tape was placed on the coated plate prior to development to provide an area of undeveloped resist for resist thickness measurement prior to development. No post-bake or etching was done. Used plates were cleaned with acetone and acid dichromate and then rinsed.

4. Experimental Design:

A two-factor experiment in which both the type of surfactant and the concentration of the surfactant in the developer was completed. An exposure-development series was used to determine the best combination under the conditions available. Analyses of film thickness loss, and image profiles and scum via Scanning Electron Micrographs (SEM), were used to determine the effect of the surfactant on the removal of image and resist scums.

RESULTS

The experiment provided valuable information on the effect of adding surfactants to a positive resist developer. As expected, the surfactants caused an increase in film thickness loss due to development. This loss increased as the concentration of the surfactant in the developer increased.

The cationic surfactant, Hyanine 1622, had a marked effect on the resist. This surfactant caused the complete destruction of the resist image. At the lowest concentration tried, .1%, the resist was completely removed and no image was visible. Even under the tape resist thickness was not measurable.

The nonionic and anionic surfactants caused an increase in film thickness loss but did not totally destroy the image. The film thickness loss increased with an increase in surfactant concentration from 0.025% to 0.5%. The results of this investigation are presented graphically in Figure 3.

The SEM's were very useful for observing the impact of the surfactants on resist imagery. Changes in line width, line shape, and cleaning ability were very visible. The SEM's also confirmed what was suspected from film thickness measurements, the images showed exaggerated standing wave

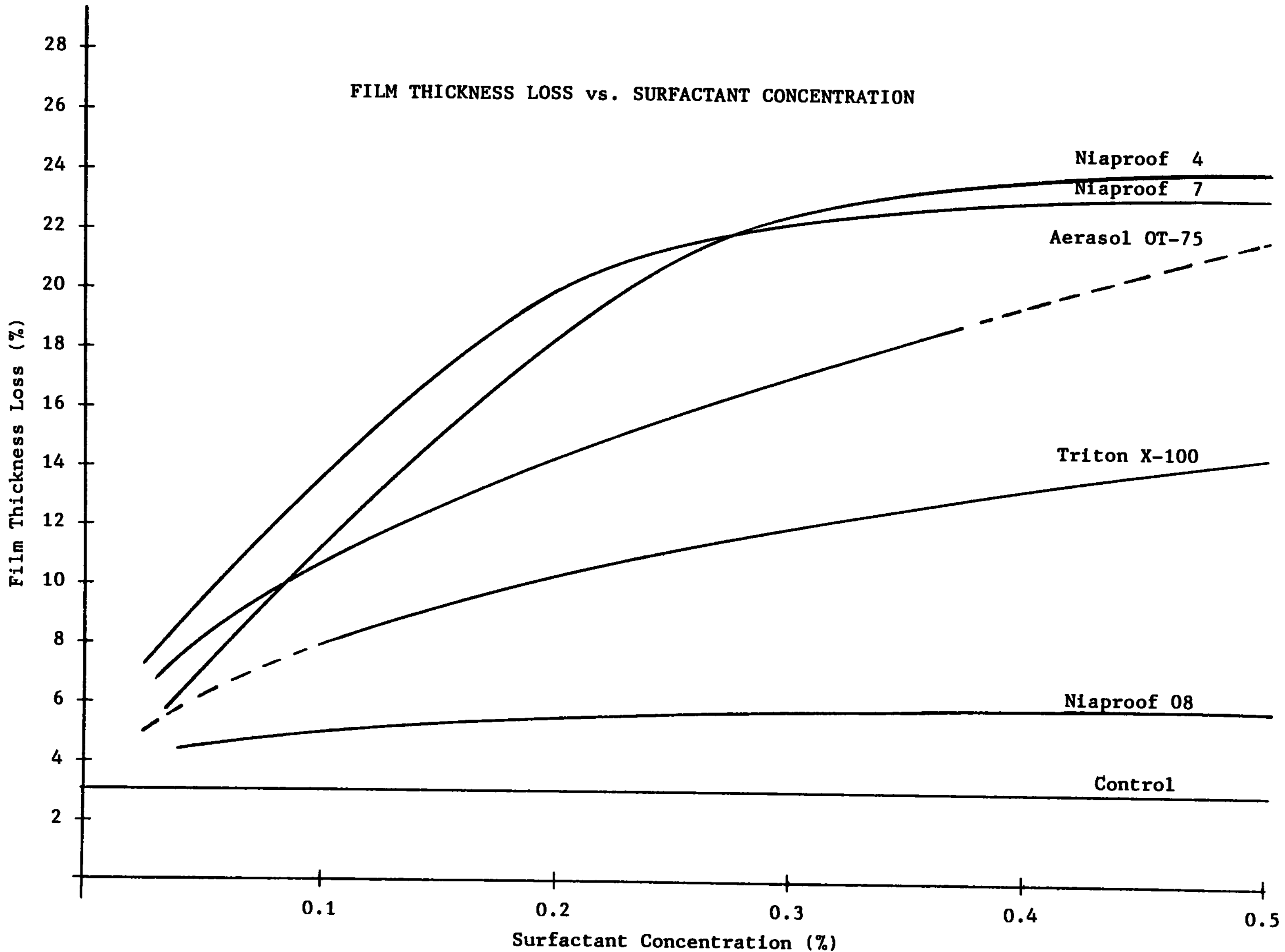

Figure 3. Film thickness loss vs. Surfactant concentration

effects. The exposing device caused considerable degradation of the exposing radiation due to the fact that it had to pass through an extra piece of glass. This exaggerated effect made image analysis more difficult.

The nonionic surfactant, Triton X-100, caused serious deformation of the 2.80 μm lines. At a concentration of 0.1% the lines were rounded on the ends and also across the lines (due to standing waves). At a concentration of 0.5% the lines were seriously deformed. The line width had been reduced to approximately 0.5 μm. Even at this high concentration the image was not clean. Impurities were visible both on the lines and on the substrate. This surfactant did not effectively clean the image.

The Niacet Corp. surfactants behaved in a similar fashion to the Triton X-100. Increased concentration caused increased film thickness loss. The Niaproof 08 surfactant produced the smallest amount of change over the range of surfactant concentrations observed. A thickness loss of 1.6% was obtained for a concentration change of 0.4%. This is very good, but examination of the micrograph showed that the reason for this small change was due to underdevelopment. The resist was not completely removed from between the lines. Increasing the surfactant concentration did not improve development; considerable scum was noted.

Niaproof 4 and Niaproof 7 both caused increases

in film thickness loss. Over the 0.475% increase in concentration, an increase in film thickness loss of 19% was obtained for the Niaproof 4 and an increase of 15.8% for the Niaproof 7. Examination of the micrographs showed that the Niaproof 4 surfactant did not provide complete development at 0.026%, while the Niaproof 7 did provide complete development, but neither effectively removed the scum at the image interface.

The fourth anionic surfactant used was the Aerasol OT-75. It preformed similarly to the Triton X-100 surfactant relative to film thickness loss vs. surfactant concentration. An 11.4% film thickness loss was observed for an increase in surfactant concentartion of 0.35%. The relationship was quite linear, as with the Triton X-100. Examination of the micrographs for the surfactant at 0.075% showed that the image was very clean. Sharp clean edges and interfaces were obtained with only a 9.5% film thickness loss. The lines were again rounded considerably and showed exaggerated standing wave effects. At 0.225% concentration the image was impaired by what looked like cracks over the entire image area. This defect is believed to have been caused by the evacuated evaporation of silver on the image for micrograph production. Apparently impurities in the silver coating caused these cracks. Except for these cracks the image appeared to be very clean; however significant changes in the image size and profile have taken place.

DISCUSSION

The experiment has clearly illustrated the impact of adding surfactants to a metal ion based positive resist developer. The concentration of the surfactant in the developer affects the amount of film thickness loss due to development. It also has an effect on the size and shape of the resulting lines. The category of surfactant used affects the type of change that occurs. The particular surfactant within a category also affects the type of change.

The initial investigation was to determine the effect of surfactant concentration relative to developability and cleanliness of the processed image.

With the cationic surfactant concentration serves no practical significance since the image was completely destroyed. With the other two types of surfactants there was a marked effect on the film thickness loss.

The nonionic surfactant produced a linear change with increased surfactant concentration. The overall change in film thickness loss was only about 6.5%, but considerable change in image profile also occurred. A lack of effective resist removal (scum) is also apparent. The surfactant addition appears to influence resist removal, but it also causes an increase in the removal of unexposed resist as well.

The images all show the exaggerated standing wave effect due to the exposing source. The lines appear to be a series of steps rather than a smooth line edge. This was a problem for making the film thickness measurements. The Triton X-100 has enough strength to destroy the images, but does not have enough strength to completely remove the undesirable materials that are on the substrate.

The anionic surfactants from the Niacet Corp., Niaproof 4, Niaproof 7, and Niaproof 08, were all sulfate compounds (chemical names are found on page 8). At the low concentrations where the film thickness loss was at a minimum, the Niaproof 08 and Niaproof 4 surfactants did not assist in producing complete development. The surfactant seemed to have some anti-wetting effects on the developer, it appears to interfere with the developers ability to get to even the exposed areas of resist. Increasing the concentration of the surfactant only causes further destruction of the line integrity in the case of the Niaproof 4, while with Niaproof 08, increases in concentration have little effect on the results. The Niaproof 7 surfactant does provide for complete development; in fact, it seems to cause overdevelopment. The lines are highly degraded, and the substrate does not appear clean.

The American Cyanamid Company's Aerasol OT-75 seems to provide the best cleaning of the surfactants tried. At a concentration of 0.075%, an excellent clean image was obtained.

As with the nonionic surfactant, the standing wave effect was exaggerated but not to the extent that the nonionic one was. Film thickness loss at this concentration was only 9.5%. This represents an increase of 6.5% over the 809 control plates. Surfactant concentrations below 0.075% were tried but SEM's were not possible. Film thickness loss at 0.03% was 6.6% an increase over control of only 3.3%.

Consideration must be given to the facilities that were used for this experiment. The darkroom temperature fluctuated considerably, and precise control of the developer temperature was not possible. Also as mentioned before the exposing device was not acceptalbe for producing the desired line quality. The spinner was not electronically controlled, and possible coating nonuniformities across the substrate could have been a source of error. This source of variation was minimized by making all the measurements from one area of the plate. Within a series, repeatability was fairly good, but between batches considerable variation was experienced.

CONCLUSION

The addition of surfactants to a metal ion type positive resist developer causes considerable change in the line dimensions and also reduces the overall film thickness of the non-exposed image areas. The Aerasol OT-75 surfactant, a dioctyl ester of sodium sulfosuccinic acid, provides good removal of impurities and scum. When the concentration of the surfactnat in the developer is kept to a minimum, the line width and film thickness changes are kept small. Further research into the ability of Aerasol OT-75 and other, anionic acids, to assist in the removal of impurities and scum is suggested. Also the use of better controllable conditions are highly suggested for further research into this topic.

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VITA

Michael P. Belden is presently studying Photographic Science and Instrumentation at the Rochester Institute of Technology. He expects to graduate with a Bachelor of Science degree in May of this year.

Mike was born in Lynchburg, Virginia in March 1960. He attended elementary school and junior high in the Amherst, New York school district. His high school education was obtained at the Antwerp International School in Antwerp, Belgium. While in high school he received a scholarship for being the outstanding senior of his class.

While at RIT Mike was a member of the varsity hockey team for four years, finishing as the only Senior of this years team. He was co-captain of the team last year.

After graduation Mike is looking to join the micro-electronics industry, but has no immediate plans at this time.