IMAGE REVERSAL TECHNIQUES WITH STANDARD POSITIVE PHOTORESIST

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Abstract

The basic reaction of positive photoresist involves the conversion of the dissolution inhibitor (diazoketone) to a dissolution enhancer (carboxylic acid). The novolac-type resin is basically unchanged, but its solubility is controlled by the presence of either the dissolution inhibitor or enhancer.

It has been demonstrated that the dissolution enhancer can be thermally degraded, and, under the proper conditions, this degradation can lead to the reversal of the resist image. It is, of course, imperative to optimize the developer selectivity and to capitalize on the specific characteristics of common positive resists to define a production-oriented image reversal process.**
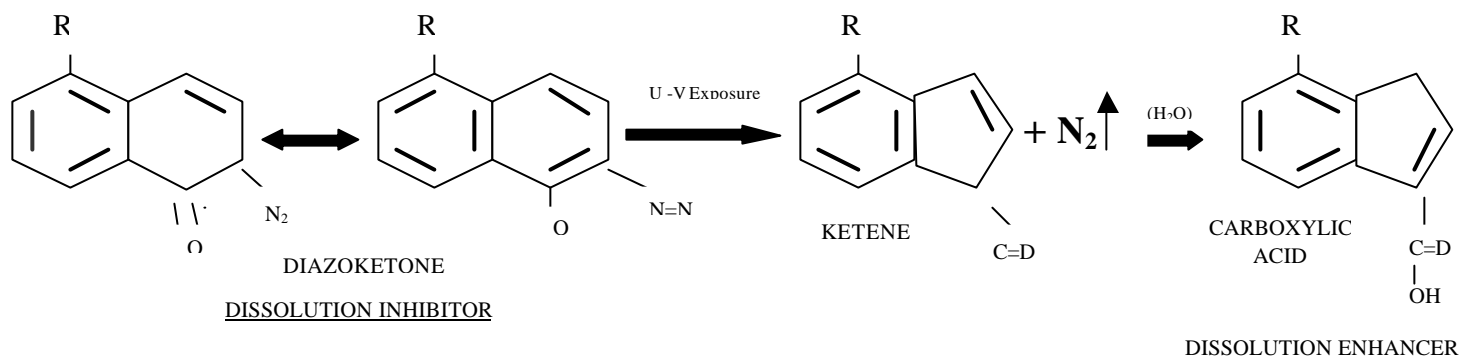
Introduction

The concept of using the same photoresist in either a positive or negative mode has long intrigued photoresist engineers, and there are several viable reasons for wishing to develop a reversal process. Optically, a darkfield mask has advantages, reducing both light scattering effects, and minimizing sensitivity to particulate contamination. Positive resist has the advantages of high contrast, good step coverage, and high aspect ratios. For many steps in the process, it is possible to use both a darkfield mask and positive resist, but for some steps, a choice must be made between the use of positive resist and the darkfield mask. The ability to perform an image reversal would permit the use of darkfield masks and positive resist throughout the process. Another possible application of the reversal process is in the situation where new products are being run with positive resist, but the retooling of older products from negative to positive masks is cost prohibitive, especially if the volume of the older products is low or sporatic. The use of the reversal process would permit the use of positive resist with the existing negative masks. A third reason for exploring the reversal process is to better understand the chemistry and reactions of positive resists. Photoresist processing has long been considered to be an art (or even akin to witchcraft) rather than a science. The number of variables which have been identified and well controlled is still less than the real number of variables, and this results in a process that is less predictable than desired. Any information that leads to a better understanding of the reactions that are possible with positive resist adds to the understanding of the system and to better process definition and control.

Theory of image reversal

Negative photoresists undergo a crosslinking reaction during exposure to ultra-violet light, creating a differential solubility based on molecular weight. Contrast is limited with this reaction mechanism. Positive photoresists, on the other hand, undergo a reaction in which the photo-active compound (diazoketone) is changed from a dissolution inhibitor to a dissolution enhancer (carboxylic acid):
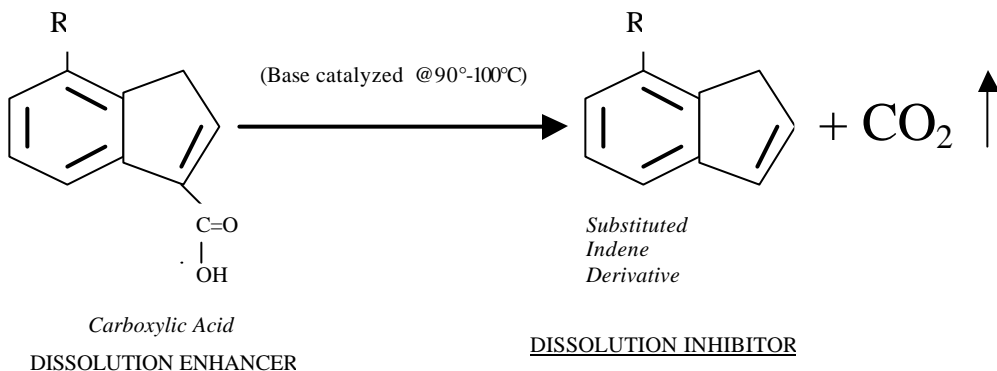
R   R   U -V Exposure   R   (H₂O)   R

$+ N_2 \uparrow$

DIAZOKETONE

KETENE   C=D

CARBOXYLIC
ACID   C=D

OH

DISSOLUTION INHIBITOR

DISSOLUTION ENHANCER

This reaction takes place under normal conditions, and trace moisture is necessary to allow the carboxylic acid to form. It is known that in the absence of this trace moisture, as in the high vacuum of an ion implanter, the ketone intermediate can crosslink with the novolac-type resin and form an insoluble polymer.[1] Other processes, including the image stabilization techniques using plasma or deep ultraviolet energies, appear to cause similar reactions, which appear to be confined to the resist surface.[2] Many of these reactions are performed without a full understanding of the chemical processes which are taking place.

Another interesting reaction of positive resist was discussed at INTERFACE ' 82 by a group of researchers from IBM Corporation.[3] They found that by adding a basic material such as monazoline, imidazole, or triethanolamine to the liquid positive photoresist, the exposed image could be reversed with a reversal bake and flood exposure. The proposed mechanism for this reaction was shown as:

R   (Base catalyzed @90°-100°C)   R

$+ CO_2 \uparrow$

C=O

OH

Carboxylic Acid

DISSOLUTION ENHANCER

*Substituted
Indene
Derivative*

DISSOLUTION INHIBITOR

This reversal reaction was found to work with about 75% resist retention, but problems were seen with product consistency and mixing techniques, as well as the potential contamination of clean resist with the additional handling and mixing.

It was discovered that the reversal process could take place without the addition of the monazoline, imidazole, or triethanolamine, although the resist retention was considerable less, and the latitude was poor at develop. Tests were panned to optimize the various process steps, with special attention given to both developer formulation and concentration.

The initial image reversal process was defined as:

1. Spin - 30 seconds @ 4000 RPM
2. Soft bake - Air dry or 30 minutes @ 55°C.
3. Expose - With pattern, 240mj @ 400nm.
4. Reversal bake - 90 minutes @ 90 °C.

5. Flood exposure - 550mj @ 400nm.
6. Develop - Bath, 60 seconds

As carefully controlled tests were begun, the reversals which had taken place with preliminary testing became inconsistent. Some wafers in a test series would reverse, others would not reverse, and still others would show only partial reversals. It became obvious that some process parameter was not being controlled , and that parameter was critical. As the various steps in the process were examined, it was seen that the time delays between process steps, caused in part by multiple wafer processing, and differing ambient conditions were responsible for the inconsistent results. It was as if the reversal reaction that took place during the reversal bake was non-permanent. If CO_2 was driven off during the reversal bake, as proposed in the IBM's paper, could it be reabsorbed ambient air during processing delays? Storage of wafers in dry N_2 after the reversal bake did indeed help to make the reversals more consistent. It was also noted that the 55°C soft bake was better than an air dry, although no densification of the resist film was expected at that low temperature. Resist film thickness after development remained disappointingly low.

Because the reaction proposed by the IBM group showed the decarboxylation reversal reaction as being base catalyzed, a step was added to the process which would expose the resist film to the vapors of a basic material prior to the reversal bake. It was felt that these vapors would effectively permeate the resist film because no densification had taken place during the 55°C soft bake, leaving the resist film fairly porous. Two solutions of volatile bases were readily available in the laboratory; KTI TMD-250, a developer containing tetramethyl ammonium hydroxide, and KTI R-10, a stripper containing triethanolamine. These were both tried, and the resulting reversals were vastly improved. It should be noted that the vaporizing apparatus was far from optimum, consisting of a black photomask box, a towel wet with solution, and a polyethylene shelf to hold the cassette of wafers. Several more sophisticated vapor systems immediately come to mind, and the potential for automating the process is high, but within the constraints of time and resources, this very simple apparatus was sufficient. The addition of a 'vapor fix' step to the initial process immediately gave consistent and predictable results.

Optimized reversal process

Once results became consistent, the task of optimizing the various processing parameters could begin. Original plans included several resists in the investigation, and KTI 809 and KTI 820 were found to reverse, but the bulk of the testing took place using KTI 1350 at a viscosity of 30 centistokes. This resist is an industry standard and has been studied extensively in numerous other projects. Later formulations, some from other manufacturers, introduced modifications including striation inhibiting agents, anti-scattering light absorbers, sensitivity enhancers, and the bonding of the resin to the photo-active compound, but the basic photoreaction remains the same. Similar process optimization testing would be advised for other positive photoresists, but corresponding trends would be expected.

Step 1. Spin: The spin speed chosen was 4000 RPM, which gave a coating thickness of 1.7 microns with a standard soft bake. Spin duration was set a 30 seconds to allow good solvent evaporation. This was felt to e important because of the low temperature soft bake that followed. Wafer size for these tests was two inches.

Step 2. Soft bake: The soft bake was performed in air at 55°C for 30 minutes. It was found that this bake was better than just an air dry at room temperature.

Step 3. Initial exposure: This is a standard align and expose process. The exposures were made on a Kasper 17A with a 200 watt mercury vapor lamp. The intensity at 400 manometers was approximately 11 milliwatts with a non-uniformity of 15%.

Step 4. Vapor fix: This step was found to be the key to repeatable and usable reversals.

Step 5. Reversal bake: During this bake, the exposed resist undergoes the reversal process, enhanced by the triethanolamine vapors, the entire resist film receives its densification bake, and any residual triethanolamine vapors are driven off.

Step 6. Flood exposure: The effect of exposure dose on the reversed image film thickness. This exposure was made with no mask, using the same Kasper 17A.

There is a very definite exposure dose required for optimum film retention. It is thought that the high dose required is due to the extended reversal bake, which may have reduced the sensitivity of the previously unexposed resist. It is not known if the 550 millijoule dose is independent of intensity, or if a different intensity level would require a different dose. The shape of the curve would suggest that the reversed image can still react to ultraviolet energy if the dose is high enough, but within the scope of this test, the latitude of the flood exposure process was not seen to be a problem, and consistent images were produced.

Step 7. Development: It was immediately seen that development parameters would be the most critical in the reversal process. A developer that was too concentrated, would result in total resist removal, and a formulation too dilute would not develop. After the vapor fix step was added, development latitude increased greatly. Four different developer formulations were found to be acceptable, but all were at a lower concentration than typically used for standard processing. All developing was done in a room temperature bath, and a standard time of 60 seconds was found to be acceptable for the R-10 treated wafers. TMD treated wafers typically required an additional 10 seconds of development. The developers and dilutions used were;
DE-3 @ 35%
TMD-250 @ 80%
Developer 351 @ 15%
Developer 312 @ 40 %
All of the initial solutions were standard product from KTI stock.

Image quality and linewidth control

Extensive evaluation of image quality and linewidth control was not possible in the time-frame of the project, but some comment is appropriate at this point. The non-uniformity of the exposure system resulted in a range of exposures on each wafer, and the quality of the photomask used was inferior t current industry standards positive process, and linewidth measurements were made. In general, the TMD-250 vapor treated wafers were not as sharp as the standard process, unreversed wafers. Edges were rougher, and at a higher magnifications, it was clear that the edges were sloped. The R-10 vapor treated wafers, on the other hand, compared quite favorably with the standard positive wafers. Development was typically clean, and edges were sharp.

Linewidth measurements was performed on a Nanoline CDC, and the results are summarized in Table 1. Variations across the wafer were smaller than expected, with the major trends

DEVELOPER	TMD-250 VAPOR	R-10 VAPOR
311 @ 40%	+ 8.8%	equal to std.
351 @ 15%	+ 4.4%	+ 1.6%
TMD-250 @ 80%	- 1.1%	- 2.9%

Table 1. Reversal linewidth variations.

being developer related. All wafers were given the same exposure doses, 220 millijoules for initial exposure, and 550 millijoules flood exposure. Although more testing is needed, it appears that critical dimensions may

be controlled by developer selection. This may be an important consideration if negative photomasks are to be used, because size adjustments are typically required.

Conclusions

It has been shown that standard positive photoresist can be used to produce negative images. The reversal process described was found to be consistent and predictable. The use of a vapor fix eliminates the need to add a base material to the liquid resist, and resist thickness after the reversal process was 90% of the film thickness before develop. The images produced with the reversal process compared favorably with those produced by the standard positive photoresist process using the same equipment and masks.

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An Improved Technique for 1/4 Micrometer Gate Length
GaAs MESFET Fabrication by Optical Lithography

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Abstract

This paper describes an innovative photolithographic method for the fabrication of 1/4 micrometer gates in gallium arsenide Metal-Semiconductor Field Effect Transistors (GaAs MESFETs). The method utilizes image reversal technology, in which negative polarity images are produced in positive diazide photoresists. This work describes improvements obtained using ammonia as the image reversal catalyst over work previously described which used imidazole [1].

The ammonia based image reversal process is characterized with respect to sensitivity to several process parameters and uniformity of the resultant linewidth. The linewidth uniformity attained using this process is ± 0.03 micrometer over a 50 mm diameter wafer and is currently used to fabricate 1/4 micrometer gate MESFETs on gallium arsenide.

Introduction

Image reversal, a technique whereby a negative polarity image is formed in a positive diazoquinone photoresist was first described by Moritz and Paal [2] in 1978. A marked surge of interest in the technique has occurred since 1982, when MacDonald et al. [3] first described the chemical mechanism.

New techniques incorporating image reversal of positive resists have been increasingly reported in the fabrication of microelectronics. Its use has recently been reported as a replacement for negative resist in the manufacture of photomasks [4].

Image reversal has several advantages over negative photoresists while eliminating many of the disadvantages. The use of positive diazide materials offers improved resolution capabilities and more reproducible processing with better critical dimension control. It uses aqueous base developers which are safer than solvents used in negative resist developers.

One additional advantage which has frequently been mentioned is its used for liftoff metallization. This paper describes a process for fabricating submicrometer gate lines on discrete gallium arsenide MESFETs. The process utilizes the liftoff capabilities in conjunction with the excellent resolution of positive resist to achieve this goal.

Image Reversal Chemistry

The image reversal process can be thought of as a three step process.

In the first step, a substrate (wafer or mask, eg.) coated with a positive diazide photoresist such as AZ 1350J is imaged in the conventional manner. Upon exposure, the sensitizer is converted to a substituted indenecarboxylic acid.

In the second step, the substrate with partially exposed resist is subjected to a post bake in the presence of a base catalyst. This causes thermal decarboxylation of the previously formed indenecarboxylic acid, rendering it insoluble in aqueous developer.

After the bake, the entire substrate is flood exposed. The resist not previously exposed now undergoes the normal conversation and is developed in an aqueous base. The portion which was originally exposed remains as a negative of the original mask.

Image Reversal for Submicrometer Geometries

Half micrometer and shorter gate lengths are essential to achieve high performance at microwave frequencies in GaAs MESFETs. The maximum frequency of operation increases as the gate length decreases. The most publicized method used to define these submicrometer lines has been electron beam lithography. This, however, requires a large capital investment. For the smaller manufacturer, the only viable alternative is optical lithography. The impetus for this work was to create a high yield reliable process compatible with small volume production.

To manufacture 1/4 micrometer gates we chose to use a "recessed gate" structure with a "liftoff" metallization process. Briefly, a "hole" in the photoresist is defined, the GaAs is etched, gate metal is deposited through the hole, and photoresist structure is washed away along with the unwanted metal.

A multilayer structure is formed with three parts. The bottom layer is a flood exposed and hard baked layer of AZ-350B positive photoresist. The middle layer is a teflon-like (PRIST) layer formed by exposing the bottom layer of photoresist to a C_2F_6 plasma [5]. The top imaging layer is Shipley 1400-24. The bottom photoresist layer is hard baked to prevent reticulation of the surface due to compressive stress caused by the plasma treatment, and the flood exposure is necessary to permit the layer to be dissolved in solvents for liftoff after metal deposition.

The wafers are exposed in a Karl Suss MJB 3HP contact mask aligner equipped with a 350W mercury arc lamp. Exposure is made with broadband illumination through a mask with 0.65 micrometer

critical dimension. Image reversal is achieved in an ammonia atmosphere at 95°C for 45 minutes in a Yield Engineering Systems LP-38 vacuum oven. Following the ammonia treatment, the wafers are flood exposed and developed in dilute Shipley Microposit 2401. This developer is used because of its ability to eroe the resulting structure to a size smaller than the original mask. Development is carried out in an immersion bath without agitation. The bath temperature is controlled to within ± 0.3°C. Development time is adjusted to customize the resultant "plug" to the desired size.

To create a structure suitable for liftoff, a layer of 1000A aluminum is deposited on the wafer. Because of the negative slope of the plug, it acts as a liftoff mask for the metal. The plugs are then lifted using resist thinner and a spray gun. As the plugs are dissolved, the metal sitting on the plug is washed away leaving a "hole" in the metal, which forms the deposition mask. This mask sits on top of the bottom photoresist which acts as a spacer layer. This resist is protected from the solvent by the teflon-like buffer layer formed earlier. The resist is etched away in an O_2 plasma until the GaAs is exposed. Once the GaAs has been etched, a metal gate can be deposited through the metal mask and the unwanted metal is lifted using standard techniques.

Experimental Description

The most critical part of this process is the formation of the plug which determines the final gate length. Several variables influence the resultant linewidth; we have selected to investigate more fully the effects of exposure an developer time.

We processed bare silicon wafers with the process described, and with a process using imidazole as the image reversal base catalyst. The processes were identical with the exception that 2.5 weight-percent imidazole was added to the imaging layer of resist and the reversal step was carried out in a convention oven at 105°C for 40 minutes. Wafers were exposed with various doses for both the imaging exposure and the flood exposure. Development was in Shipley Microposit 2401 concentrate diluted 1:6 with deionized water. Develop times were varied to determine the erosion rate of the plug. Linewidth measurements were made on a scanning electron microscope.

Results

Table 1 summarizes the results of an experiment using ammonia in which we varied flood exposure dose and develop time. In each case 9 measurements were made at equally spaced locations across the wafer and standard deviation was calculated. Constancy in standard deviation, independent of development time, indicates that variations are due not to erosion, but to other factors which we will discuss later. In order to remove the effect of variations in the linewidths of various mask plates, we plotted linewidth differences at each dose. The effect of flood exposure dose appears negligible.

The constant erosion rate of approximately 70 A per second implies that the sensitizer is completely converted during the first exposure and there is none remaining in these areas to affect development. The data were then normalized to a 75 second development time and replotted to determine the significance of the exposure does. The main effect of increasing exposure us in increase the size of the initial plug before erosion takes place; however, this effect is much smaller than the effect of erosion by developer.

The erosion rate for this process is 65% greater, 120 A per second.

Discussion

We have found many variables that affect the final linewidth of the plug, eg. Developer concentration and temperature. We have attempted to minimize the process variations by carefully controlling the critical variables. There are also several modes of failure that can occur during the formation of the plug. The large

aspect ratio of the plug, typically 3:1 for 1/4 micrometer gates, makes it mechanically unstable. Because this plug sits on a teflon-like layer, adhesion of the plug is sometimes poor enough to cause a straight line to become bowed. The plugs can also fall over and break. These types of failures are minimized by careful control of process parameters. No agitation is used during development to avoid undue mechanical strain of the structure. Also, the time required to form the PRIST buffer layer and the thickness of the imaging photoresist are both adjusted to assure maximum stability.

Another mode of failure which is inherent in the process occurs during the plug lift step. Once the plugs are dissolved in the solvent, the metal which was on the plugs falls onto the wafer. Unless it is mechanically washed away it will remain where it falls. If it falls on a gate structure it can cause a catastrophic failure of that device. We have minimized this problem by using special materials for the metal mask using a spray gun to remove the plugs. The loss from all these failure modes has been reduced to less than 5%.

The most significant factor over which we have little control is the contact between the mask and the wafer. Particles on either the mask or the wafer cause loss of contact in the area surrounding the particle. This affects the distribution of light in the local area, causing linewidth variations. This may be avoided by using projection printing where the aerial image can be better controlled.

While uniformity on a wafer is very good, there can be differences from day to day. For this reason we monitor linewidth in process an SEM to assure consistent results. Although this is time consuming, it makes the process very reliable. We are able to print gate lines with a variation of less than 0.03 micrometer from day to day. We have successfully used this process on more than 400 experimental wafers and on 50 1/4 micrometer and 1/2 micrometer GaAs MESFET wafers.

Acknowledgements

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Table 1

Wafer Number	Developer Time (sec.)	Average Linewidth (microns)	Standard Deviation (microns)
1	45	0.563	± 0.026
2	45	0.608	± 0.021

3	45	0.588	± 0.018
4	45	0.627	± 0.031
5	60	0.465	± 0.029
6	60	0.543	± 0.011
7	60	0.498	± 0.029
8	60	0.525	± 0.032
9	75	0.371	± 0.019
10	75	0.448	± 0.026
11	75	0.399	± 0.026
12	75	0.433	± 0.019

Average standard deviation 0.023 ± 0.006