IMAGE REVERSAL OF POSITIVE PHOTORESISTS

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LAB REPORT FOR PHYSICS 134

ADVANCED PHYSICS LAB

(TAKEN AS PHYSICS 199)

UNIVERSITY OF CALIFORNIA,

SANTA CRUZ

DEPARTMENT OF PHYSICS

WINTER QUARTER, 1987

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This paper will report on laboratory work done at Raytheon Co., Research Division describing a series of experiments I conducted verifying the validity of image reversal as a technique to produce the repeatable and controllable photoresist profiles needed for a metal "liftoff" process. The results will be generalized as needed in order to avoid releasing any propriety information, thus the actual use of this process at Raytheon will not be discussed. What will be discussed is the rationale for using a liftoff process for the metallization of semiconductor devices, positive resist mechanisms, the theory of image reversal and its relevance to liftoff.

POSITIVE PHOTORESIST

Positive photoresist is a three-component mixture of an alkaline soluble novolac resin, a photosensitive dissolution inhibitor, often called the Photo-Active Compound (PAC) and a carrier solvent. The PAC serves to retard the dissolution rate of the novolac resin in alkaline solutions. When exposed to light of sufficient energy and the proper wavelength (between 300nm and 450 nm), the PAC will undergo photochemical decomposition which renders the polymer soluble in an alkaline developer. The chemical mechanism is as follows: The PAC is a diazoketone which upon exposure to ultraviolet (UV) radiation generates a highly reactive intermediate ketene and liberates nitrogen. The ketene will react with available water to form an indene carboxylic acid which is now soluble in the basic developer. The differential solubility rate between exposed and unexposed areas (~1,000 to 1) allows the transfer of the images of circuit elements from a patterned glass photo-mask into developed resist images with tight control of their physical dimensions. This is called positive photoresist because the clear areas of the mask remain as clear areas in the photoresist, a positive image. The novolac resin remains basically unchanged by this reaction yet its solubility is controlled by the presence of either the dissolution inhibitor (PAC) or the enhancer (carboxylic acid).

A typical positive photoresist consists of 70% solvent, 8% PAC and 22% resin. The molecular weight and exact percentage of solids is tightly controlled to assure exceptional film thickness uniformity. The photoresist, which has been filtered down to 0.2μm, is applied onto the semiconductor substrate and spun at between 3,000 and 6,000 RPM. Spinning removed the bulk of the solvent and distributes the resin uniformally over the surface. Thickness uniformities of ±5% for a 2 μm film on a 6 inch silicon wafer are typical. The final thickness is determined by solids content and spin speed. The substrate is next baked, either in a 90°C oven or on a hotplate to remove the remaining solvents and to densify the resist. The wafer is now ready for exposure.

The wafer is processed in an "aligner" which holds the mask over the wafer allowing translational (X-Y) and rotational (θ) control. The aligner also provides an optical microscope for precise alignment of the pattern to the previous patterns. This way all the circuit elements are built up one at a time, each step consisting of patterning the photoresist and performing some function: a chemical etch, an ion implant, or a metallization. A typical silicon MOS process will consist of perhaps 10 to 15 masking steps. Once the wafer is aligned, the mask and wafer are constrained from movement and exposed by a UV source, typically a high pressure mercury vapor lamp. The lamp has a precise shutter allowing for tight control of the actual energy delivered to the wafer. Optics are used to provide uniform (±5%) exposure over the entire wafer. The exposure can be controlled and set because the aligner is designed to maintain a constant intensity (typically

10 to 100 mWatts/cm^2) and the shutter is controlled by an accurate timer. Typical exposure energies are around 50 - 100 mJoules/cm^2. In order to have a repeatable and controllable process, the following variables, once optimized, must be maintained: UV energy (determined at the proper wavelength, typically 400 nm), resist thickness, mask contact pressure, ambient temperature and humidity (typically the humidity is maintained at ~ 40% in order to assure the necessary levels of water required to produce the carboxylic acid). The normality of the developer, the temperature the time of development must also be tightly controlled. The work is typically performed in a "clean room" where low particulate levels are maintained. Because the geometries being produced in the photoresist can be on the order of one micron in size, the air must be filtered to avoid high particle concentrations, which upon contact with the wafer, would alter the patterns in the resist (pinholes, voids, etc.) A typical Class 100 clean room would guarantee that there exists less than 100 particles of 0.5 μm or above per cubic foot of air.

The dissolution rate of positive photoresist is a non-linear function of the exposing energy. UP to a certain critical value of exposure energy (E_i), only a small amount of resist is lost (less than 10%). Once this threshold is crossed, the exposed resist rapidly dissolves until at a second critical value (E_0), all the resist will be dissolved. The increment value this energy spans is related to the contrast of the resist process. A high contrast photoresist process is characterized by a large "gamma" (?) value as defined below:

NORMALIZED (EXPOSED)
PHOTORESIST THICKNESS

LOG EXPOSURE
ENERGY (mJ/cm^2)
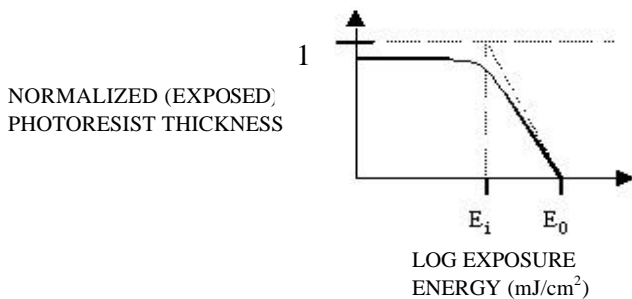
$$? = [\log_{10}E_0/E_i]^{-1}$$

Where E_0 is the energy where the exposed resist is completely removed and E_i is the threshold energy where the exposed resist first experiences significant removal (extrapolated back to zero initial resist loss. Thus ? is the slope of the linear tail of the curve where the resist experiences significant resist loss. A higher gamma also related to the sharpness of the resist profile. Typical ? values range from 1 to 10.

Linewidth control is also affected by exposure energies and gamma values. The higher the contrast (Y), the more accurate the transfer of mask dimensions into the photoresist is for a given exposure energy. Due to diffraction effects, the resist openings tend to enlarge when exposed to energies much greater than E_0. A well controlled and optimum photoresist process should produce deviations from the mask of less than 10%. Linewidth and resolution are also related to the mask to photoresist separation, again due to diffraction. The ability of an exposure system to resolve a periodic set of equal lines and spaces is related to the exposing wavelength and separations as follows:

$$2b_{min} = 3[?(s+1/2d0]^{1/2}$$

where b_{min} is the minimum resolvable set of lines and spaces, s is the separation between mask and the top of the photoresist, d is the resist thickness (~2 μm), and ? the exposing wavelength (~400 nm).[6] For "hard" contact printing (s=0), the minimum resolvable b is ? 1 μm, and for a proximity print with a gap s = 10 μmm b ? 3 μm.

THE LIFTOFF PROCESS

Liftoff processing is often refereed to as an "additive" process in contrast to the more typical use of a photoresist mask where the areas of desired metallization are protected and the undesired areas are left exposed and etched away using and appropriate chemistry. In a liftoff process, the substrate is covered by photoresist everywhere except in areas where the metallization is desired. The metal is then added, covering the entire substrate with the metal sitting on top of the photoresist and in contact with the substrate in the open areas. The photoresist is subsequently removed lifting the unwanted metal away from the substrate, leaving behind the desired metal pattern.

The impetus for a liftoff process the need to pattern metal lines on semiconductor substrates where the use of chemical or plasma etching is either undesirable or incompatible with the process or materials involved. An example of this would involve processing on GaAs substrates. Typical metallizations schemes require the use of a metal composite to form contacts and transmission lines. Typical metals used are Aluminum, Gold, Nickel, Platinum, Tantalum, Titanium and perhaps others, where the required contacts may use two or three in some combination. Etching these metals would require very harsh chemicals that would severely attack the GaAs substrate and degrade the performance of the semiconductor.

The other primary need for liftoff processing is when tight linewidth control is required. Typically, a chemical etch is isoptropic in nature (i.e., etches equally in all directions). Due to processing related deviations, metal films typically have thickness variations across the wafer. Film thickness variation requires the wafer be "overetched" in order to assure complete etching has occurred. This translates into line widths being reduced when the isotropic etch works under the resist mask. The most severe case occurs where the film thickness is least. Because the liftoff process depends only on the control of the photoresist, linewidth is maintained independent of metal thickness or variations in the etch process.

Liftoff was first introduced as a "brute force" technique. The idea was a thin metal coating (~ 0.2 μm), was deposited over a thick (~2 μm) photoresist pattern, forcing the metal to make a clan break. Unfortunately this idealized process can not be practically realized. First, it requires the metal to be delivered normal to the semiconductor surface. The best approximation to this situation would occur in an evaporator. The metal "melt" sits in a water cooled crucible inside an evacuated chamber (typically in the 10^{-6} to 10^{-8} Torr range) where an electron beam is directed via a magnetic field to impinge on the metal surface, heating the metal in a controlled manner. Due to the elevated temperature of the metal melt, a vapor pressure is created allowing the metal atoms to diffuse throughout the chamber, as if from a point source. If the substrates are suspended at a sufficient distance, and aligned tangent to the parabolic curve of a dome, the metal atoms tend to arrive normal to the surface. In reality, constraints tend to limit the realization of this phenomena. Wafers tend to be quite large, ranging form 3 to 8 inches in diameter (for silicon substrates) so only a small portion can be tangent to the required curve. Practical considerations also tend to limit the assembly of this commercially available equipment all making an ideal evaporation impossible to achieve on a production scale. In reality what happens is the metal will build up on one of the walls of the photoresist. When the photoresist is subsequently removed, this buildup can remain, a condition known as "winging". Winging metal tends to short subsequent metallizations, reducing yields. Still other metallization schemes tend to be worse. Sputtering, which is more conformal than evaporation (it is an extended source) and chemical vapor deposition of metallic films a highly conformal process, will complete cover the photoresist and impede its

removal. This implies that a different resist profile is needed in order to assure the high yields required from photolithographic steps.

The second major obstacle to a brute force approach is the resist profile itself. Because photolithography is an optical process, it is subject to optical constrains. The ultraviolet light will be absorbed as it passes through the film causing the top of the film to receive a higher dose of energy than the bottom, making it more soluble in the developer. This produces resist profiles that instead of being at right angles to the substrate, form more rounded structures, larger at the bottom and smaller at the top. In addition to absorption, diffraction also pays a significant role in creating positive slopes allowing the light to spread out and expose a larger area at the surface of the resist, a typical requirement in order to avoid damaging the mask and the wafer. As the gap increases, the profile becomes quite rounded and resolution is reduced.

In order to bypass these limitations and develop a controllable, repeatable liftoff, a variety of processes have been developed in order to modify the positive resist profile or to develop complex double and triple layer structures whose primary goal is to create a negative sloped (or undercut) profile. IBM, in the summer of 1980, introduced the first single layer liftoff process that employed profile modification.[1,2,3] The photoresist is exposed normally and soaked in an aromatic solvent, typically chlorobenzene. The penetration of the solvent into the resist is controlled by the soaking time. The previously exposed areas, where penetrated, tend to dissolve slower than the un-penetrated areas under normal development. Thus, if the un-penetrated resist is over-developed, an undercut structure is obtained. This process proved in the long run to have a small process latitude and to be very expensive to implement. The poor process latitude appears to be a function of the sensitivity of the resist structure to a wide variety of variables. These variable include exposure energies, developer concentrations, temperature, time and especially trace impurities in the chlorobenzene. A small variation in any of these variables tended to be catastrophic.

Other approaches to produce liftoff profile involved complex multilevel structures. A typical structure consists of a bottom layer, perhaps Poymethylmethacrylate (PMMA), a photosensitive resist formulation different from the usual diazo-type photoresists, which is coated with a positive photoresist and exposed/developed normally. Because the PMMA is not sensitive to normal (400 nm) UV exposures, it remains essentially intact. The top resist layer now forms the mask for exposing the bottom layer, typically at a wavelength around 200 nm. By over-developing the PMMA (the developer used has no detrimental effect on the top resist layer), an undercut structure produced. Problems occur at the interface of the two resists which tend to intermix in an uncontrollable manner. Problems also occur due to the softbake step used to cure the top resist affecting the bottom resist. Tri-level structures have also been developed where the interface between the two resist is separated by a dielectric (SiO_2 or Si_3N_4) film or even a metal. This requires an additional etch step to remove the intermediate layer before exposing the bottom layer of photoresist. This bottom layer can also be a non-photoactive layer, like polyimide, which is simply etched once the intermediate layer is patterned.

IMAGE REVERSAL

Given the complex nature of the above approaches, which impose additional cost to the process and still tend to be lower yielding than conventional photoresist processes, work continued to find a simple, controllable, high yield liftoff process. In 1975, the basic principles of image reversal were first introduced. It was found that the addition the chemical Monazoline®,[4] whose functional core is five-cornered imidazole ring, could be used to catalyze a reversal reaction.[5] When this positive photoresist mix is exposed to the UV light, producing carboxylate salt. Heating the resist prior to development (~100°C) will cause the salt to decay, releasing CO_2 and transforming the molecules into a non-acidic form which is poorly soluble in the basic developer. The previously exposed regions are now as insoluble as the unexposed regions, yet contain

no photoactive compounds to react in subsequent UV exposures. A flood exposure (i.e. UV exposure without a mask) is used to expose the areas previously un-reacted, which when developed, create a negative image of the original mask. Thus, the positive resist is reversed and functions as if it is a negative photoresist. The most important consequence of the reversal process the liftoff, is that not only the tone of the resist is reversed but the slopes as well. What was originally a positive slope is now a negative slope, exactly a desired for liftoff.

It was later shown that the decarboxylation reversal process could be achieved by subjecting the resist to a wide variety of basic solutions.[6] The problems encountered with additives were many, making repeatable process development difficult. Additives introduced the potential of particulate contamination, were difficult to mix homogeneously, and had short lift spans (typically only several hours due to reactions with the air). Or particular importance was the discovery that the reversal can be achieved by baking the resist coated substrates inside an oven in the presence of a basic vapor. This vapor diffuses into the film initiating the decarboxylation reaction in the previously exposed regions. Because the reaction is a diffusion process, it can be easily controlled by maintaining constant temperature and vapor pressure. Two commercially available image reversal system are presently on the market. One system, by a company called Imtec, delivers the vapor pressure from an amine liquid source into a vacuum oven. A second system, by Yield Engineering Systems, Inc (Y.E.S.), simply delivers anhydrous ammonia (NH_3) into a vacuum oven. The advantage of the ammonia system is easier control of vapor pressure and the absence of residual water vapor which will react with the NH_3 producing NH_3OH, a corrosive to the system, thus creating contaminating particles. It is the Y.E.S. Image Reversal system which will be used in the actual experiments.

EXPERIMENTS

The objective of the following experiments was to verify that an Image Reversal process, adopted from another group here at the Research Division, would give the proper resist profiles needed for metal liftoff processing on semiconductor substrates. The process must be capable of being used on a routine basis, in a repeatable and controllable manner. Of major concern was the slope and repeatability of the photoresist profiles, and if the process will provide adequate control of critical dimensions (deviations of metallized line width from mask dimensions). Part 1 of the experiment will look at the resist profiles produced using the transferred process and comparing this to the resist profiles produced from using hard contact and the tri-level process previously described. Part 2 will consist of finding the optimum baking conditions, and verifying the results with photomicrographs taken from a Scanning Electron Microscope (SEM) plus verifying linewidth control by measuring mask features and comparing to the corresponding metallized lines after evaporation. Part 3 looks briefly at the type of photoresist profiles produced when a proximity process is used.

EQUIPMENT

The following equipment was used for the experiments:

? ? A photoresist "Spinner" which holds the substrates on a vacuum chuck and accurately maintains constant RPM for a specified time after dispensing the photoresist (the conditions used for all the samples was 4,000 RPM for 30 seconds).
? ? A 90°C convention oven (for softbaking the resist to remove the remaining solvents).
? ? A 90°C hotplate (an alternative to the softbake oven).

- ? ? An Aligner designed for micron accuracy alignments on up to 3 inch substrates. The system exposes the resist using a high pressure mercury vapor lamp, holding constant intensity at 400nm.
- ? ? A constant temperature bath to maintain the developer temperature at 21°C ± 1°C.
- ? ? Y.E.S Model 310 Image Reversal System.
- ? ? A computer controlled E-Beam evaporation system (Aluminum was used to metallize the samples).
- ? ? An optical microscope capable of 50X to 1,000X magnification.
- ? ? A Scanning Electron Microscope (SEM) capable of the non-destructive examination of photoresist coated substrates at low voltages, eliminating the need to coat the samples with gold in order to prevent charging. Magnifications range up to 30,000X.
- ? ? An optical linewidth measuring system for C.D. measurements.
- ? ? A photometric radiometer to measure the UV exposure energies.

MATERIALS

The following materials were used:

- ? ? Three (3) inch GaAs semiconductor grade substrates.
- ? ? Shipley S1400-31 Positive Photoresist.
- ? ? Shipley CD-30 Positive Photoresist Developer (Alkaline Normality = 0.30).
- ? ? Ultra-High Purity Anhydrous Ammonia (NH_3) gas.
- ? ? Semiconductor grade Acetone for stripping photoresist during Liftoff.
- ? ? Semiconductor grade Deionized (DI) water used for rinsing.
- ? ? Various photomask levels as required.

RESULTS

PART 1

A set of three inch GaAs substrates (called "wafers") were coated with S1400-31 positive photoresist at 4,000 RPM for 30 seconds and softbaked on a 110°C hotplate for 45 seconds (final film thickness of 2 μm). The wafers were exposed using an arbitrary photomask level at an energy of ~ 200 mJ/cm^2 (measured at 400 nm). The wafers were next processed in the Y.E.S-310 Image Reversal system. The process takes place inside al large vacuum oven which provides excellent temperature uniformity (±2°C). the system pumps down into the range of ~ 1 torr, and purges up to near atmosphere, using heated N_2. This process continues through several cycle in order to remove any excess water from vapor form the system and to assure temperature stabilization. Next, the anhydrous ammonia (NH_3) gas is introduced and set to maintain the system at 700 torr (just below atmospheric pressure to prevent the gas from leaking out), for 45 Min at 90°C. During this time, the NH_3 will diffuse into the photoresist film and neutralize the carboxylic acid, initiating the reversal process. The system finally pumps down and back fills with N_2 seven times to clean out any residual NH_3 making it safe to open up the system.

The wafers are next flood exposed (no mask) at an energy of ~ 1,000 mJ/cm^2. The flood exposure gives a second degree of freedom to the process. The first exposure has a strong effect on the undercut profile (because the image reversal process is simply reversing the original profile) but it also has primary control of the linewidths. In this process, the need for linewidth control has determined the first exposure energy. The

flood exposure, a variable which has only weak control of the undercut, is actually used to control the profile. This is why such a large exposure energy is needed on the second exposure.

The wafers were developed for 90 seconds in Shipley CD-30 Posistive Photoresist Developer, at 21°C, rinsed in DI water, and dried. Aluminum (1,000 Å) is deposited in the E-beam evaporator onto the wafers which will be cleaved through the structures for examination in the SEM.

PART 2

The above process worked well and was repeatable, so work continued. Due to temperature restraints on the semiconductor substrates typically used in our group, it has been determined that 90°C is the maximum temperature the wafers should be subjected to in process. Thus the 110°C hotplate bake needed to be changed. There were two choices, a 90°C. Wafers were processed as before, with some receiving an oven bake times were chosen because 3 min on a hotplate gives an equivalent densification as the 30 min oven bake. The 2 and 4 min values are used to show how much process latitude there exists in the process. The oven bake clearly gave a more rounded profile at the top with less of an undercut. The hotplate bakes all looked very good and equivalent. Thus, if the wafers are softbaked for 3 min at 90°C, even a ± 1 min deviation will not adversely effect the profile. In order to test the linewidth control, several wafers were coated with metal and lifted off in acetone. The wafers were next measured in an optical linewidth measuring system along with the corresponding features on the mask. Many areas were measured across the wafer (20-30), averaged, and compared to the average readings from the mask. The linewidth control for the hotplate was essential indentical for the three temperatures, again showing the wide process latitude. Although the linewidth control was better for the oven baked samples, the 3 min hotplate was acceptable and based on the superior liftoff profile, was adopted as the actual softbake temperature for all future processing. This process has a gamma (?) value of 2, which is typical for his type of photoresist.

PART 3

The final point of investigation was the effect of exposing wafers in proximity. In the standard photoresist process, photoresist slopes tend to become more rounded as the separation increases, but the image reversal process should still be able to provide undercut profiles. It is desirable to use a proximity process whenever possible, because it prevents the mask and wafer from touching each other, preventing is the need for using contact printing to provide the needed resolution. A typical photomask costs ~ $1,000 and has a very shortened life span (perhaps 50 to 100 expousres), when used in contact. This is fine for an R & D process, but the ultimate goal of any research it to transfer the process into production. A large scale production can process hundreds of wafers a day, necessitating the replacement of the mask every day!

CONCLUSIONS

This set of experiments has demonstrated the image reversal technique to be a repeatable and controllable process when liftoff resist profiles are required for the metallization of semiconductor substrates. It was found that a 90°C hotplate bake for 3 min gave the desirable profiles and linewidth control. It was also shown that a proximity process is also feasible (and indeed, desirable).

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