George G. Collins
Cary W. Halsted

Process Control of the Chlorobenzene Single-Step Liftoff Process with a Diazo-Type Resist

Introduction of the single-step chlorobenzene liftoff process using a diazo-type resist to manufacturing lines produced problems not encountered during development and pilot-line work. Variances in the structure of the photoresist liftoff image are the result of complex interactions among exposure, chlorobenzene soaking, development, and post-application baking conditions. Effects produced by these variables can be controlled by monitoring the linewidth, overhang, and height of the liftoff resist structure using a scanning electron microscope (SEM). Loss of resist thickness during the chlorobenzene soak is used instead of penetration, as measured on SEM photographs, to monitor the soaking process. Data are presented on the creation and stability of the overhang structure, the process controls required to achieve that stability, and the interactions among the process variables. The process, as practiced in a manufacturing mode, was found to have greatest reproduceability at low exposure, with a combination of long soaking times and high post-application baking temperatures.

Introduction

The photoresist liftoff process was introduced to semiconductor manufacturing as an improvement in metal pitch for high-density arrays. Liftoff processes accomplish this improvement by eliminating the etch bias component of subtractive etching.

When the chlorobenzene single-step liftoff process, using a diazo-type resist, developed by Hatzakis, Canavello, and Shaw [1], was introduced to IBM semiconductor manufacturing, it replaced a two-step process that required the evaporation of a thin silicon layer between two layers of photoresist [2]. In the two-step process, the overhang of the liftoff structure was created by first patterning the top photoresist layer with conventional ultraviolet exposure tools and then etching the pattern in the silicon film. Blanket exposure and development of the bottom photoresist layer produced the overhang. While the overhang cound be consistently produced, the use of three films created a tremendous sensitivity to particulate defects and was not compatible with the manufacturing yield requirements of the IBM 64K dynamic random access memory (RAM) chip [2].

The chlorobenzene process offered relief from sensitivity to particles; however, the process was more susceptible to particulates than subtractive etching because the metal was evaporated over a resist structure. Contamination introduced at any point in the process can create metal defects during liftoff.

The rapid development of new products and processes which typifies the semiconductor industry often necessitates completion of new process development after introduction to manufacturing. The complex interactions of the process parameters in the single-step liftoff technique make a complete understanding of the effects of the manufacturing environment and tooling variables necessary before the process can be utilized effectively. Although the single-step chlorobenzene process was successful in the pilot-line operation, it became evident, after the process was introduced on manufacturing lines, that the larger tool set was creating variations in the liftoff process that made control of the overhang structure very difficult. Thus, it was necessary to determine how each process step affected the overall structure, as well as the rate of change of the structure. This paper discusses the important process variables involved and their optimization.

All known process variables were monitored by satellite computers and each wafer was tracked through the process sequence, producing data channeled to a host computer [3]. Inspection data on each wafer could be compared to the process tool and to process parameters used to manufacture that wafer. Problems were identified with particular tools, and existing variations of the process parameters were analyzed.

While process development work on a manufacturing line presented obvious difficulties, the use of the computer data base allowed the manufacturing engineer to analyze multiple perturbations simultaneously. This led to the understanding that the post-application bake, initially considered to be of minor influence, was a prime controlling variable.

Liftoff structure

In the chlorobenzene process, wafers receive standard photoprocessing with diazo-type resists, such as ®AZ-1350J [4], with the addition of a ten- to twenty-minute soak in chlorobenzene prior to resist development. As used in the manufacture of IBM SAMOS products, the chlorobenzene soak takes place after exposure of the mask pattern using projection printers, and before development. After the liftoff pattern has been developed, aluminum is evaporated on the wafer. Liftoff of the unwanted aluminum is effected by dissolving the resist pattern in N-methyl pyrrolidone.

The liftoff structure is shown in Fig. 1. The desired resist structure must be taller than the thickness of the aluminum to be evaporated in order to eliminate bridging of the aluminum on the wafer to the aluminum on top of the resist. The structure should have a small overhang (the top of the resist line larger than the bottom) so that the aluminum is not evaporated on the sidewalls of the photoresist, and yet the overhang should be large enough to ensure consistent liftoff. The chemistry producing this shape is described by Hatzakis [1]; the detailed mechanism of the soaking process is discussed in the companion paper by Halverson *et al.* [5], and thus is not repeated here.

The major problems encountered on the actual manufacturing line were maintaining an overhang structure that was stable to further processing, and obtaining correct image sizes from day to day. The process experiments investigated parameters, such as exposure, chlorobenzene soaking time, development time, and resist baking temperature, which affected the size and shape of the liftoff structures. All experimental wafers were cross-sectioned for measurement of the resist structures by means of scanning electron microscope (SEM) images. Three different widths and two heights were required to define the process influences on the structure. These measurements were then compiled in an APL data base matched to the processing parameters. Single-variable comparisons on hundreds of data points generated equations useful in defining structural dependencies on these process parameters. Figure 1 defines the terms used in this paper which relate to the liftoff structure. The resist linewidth Z and height A are governed by individual product needs, whereas the overhang O is a process concern only.

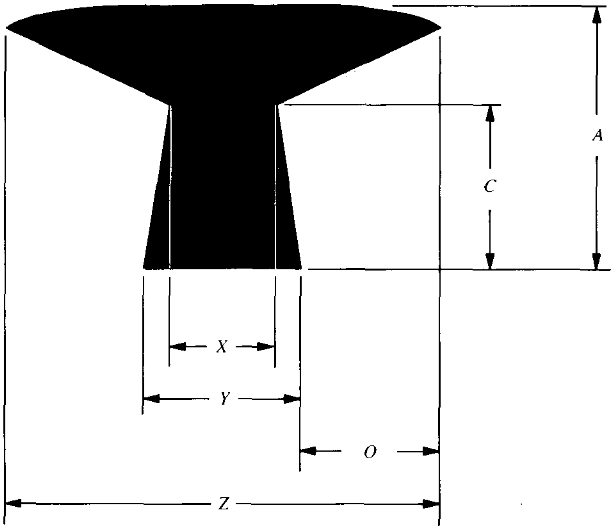

Figure 1 The overhang structure showing the relevant dimensions for the height A, the neck height C, the neck width X, the foot width Y, the linewidth Z, and the overhang O. Penetration is defined as $(A - C)/A$, and the overhang as $(Z - Y)/2$.

The remainder of this paper is organized to show how the final liftoff structure (linewidth, overhang, and height) is influenced by the process variables (exposure, soaking time, development time, and resist baking temperature).

Development rates

The chlorobenzene soak and pattern exposure created four unique regions within the photoresist, as shown in Fig. 2(a). Exposed and unexposed regions have unique average development rates D_{ue}, D_{se}, D_{uu}, and D_{su}. The subscripts are defined as follows: ue = unsoaked exposed region, se = soaked exposed region, uu = unsoaked unexposed region, and su = soaked unexposed region. The development rates are increased by exposure and decreased by soaking in chlorobenzene; $D_{ue} > D_{se} >> D_{uu} > D_{su}$.

The beginning stages of the development process are illustrated in Fig. 2(b). Fast development occurs in the exposed region; this accelerates as the chlorobenzene-soaked

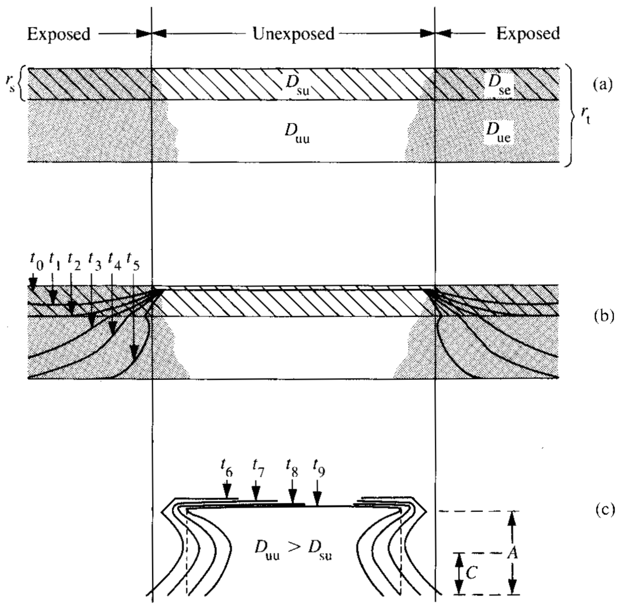

Figure 2 (a) The resist structure after exposure and soaking in chlorobenzene. Four regions are defined, each with a unique development rate D (see text). (b) Initial stages of development in the exposed region. Note the accelerating development rate in the unsoaked region. Soaking times t increase in the order $t_0 < t_1 < t_2, \cdots$, etc. (c) Development in the unexposed region and formation of the resist overhang structure.

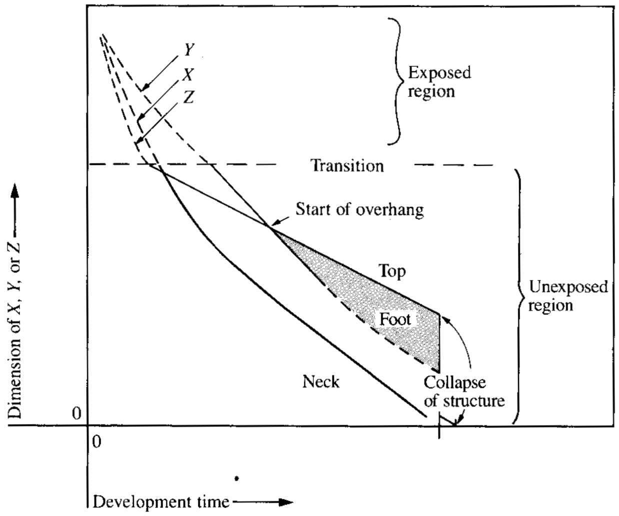

Figure 3 Changes in the development rates for the widths of the top Z, the foot Y, and the neck X as functions of the development time in both exposed and unexposed regions.

region r_s is passed. At this point lateral development of the unexposed regions begins. As the development process continues, all of the exposed resist is dissolved, and the formation of the undercut proceeds because of the slower development rate of the soaked resist in the unexposed region. Figure 2(c) illustrates how the image is continually shrinking during creation of the overhang. Note that the soaked region is being developed from both top and bottom surfaces. This creates an illusion that the soaked region r_s becomes proportionately thinner with respect to the final resist thickness r_t. (Note that r_t is not equal to A, since A is measured *after* development.)

The shape of the liftoff structure responds to processing changes that affect D_{ue}, D_{se}, D_{uu}, D_{su}, or r_s. Changes in the exposure or development conditions can be monitored by SEM pictures of the resist structures. However, changes in the original soak-layer thickness r_s are more difficult to follow because the soak layer can be observed only *after* development, when it has been thinned by an undetermined amount. Thus, a post-processing soaked-layer dimension r'_s is measured, not r_s.

Figure 3 depicts the dependence on development time of the individual parameters which determine the overhang structure. The development rates of the linewidth Z, the neck width X, and the foot width Y in the partially exposed (*e.g.*, by scattered radiation) region proceed rapidly until the completely unexposed region is reached. The transition point can be seen by inflection points for the curves in Fig. 3. Once the unexposed region is reached, the differences in the three development rates increase. In the unexposed region, the faster development rate in the unsoaked regions (reflected in the neck and foot dimensions) translates to a more rapid decrease in neck and foot width than in the top linewidth. The crossover point of the top and foot defines the start of the overhang. When the neck width approaches zero, the structure collapses. Note that the development rate of the foot decreases with increasing distance into the unexposed region. The observed curvatures of the foot and neck are a measure of this partial exposure of the unexposed region.

Penetration

A penetration parameter has commonly been taken from SEM cross sections to measure the depth of chlorobenzene penetration during the soaking process. *Penetration* is defined as the ratio of the apparent soaking thickness to the total height on a *developed* image, $(A - C)/A$. This parameter is discussed further in the section on soaking conditions.

Exposure

The first experiment used to help understand the complex dependencies of the overhang structure on processing parameters was to vary the exposure conditions and observe various *developed* structural features under constant soaking conditions. These features included the linewidth Z, the overhang O, and the developed resist thickness or height A.

Linewidth

Figure 4 shows the observed rate of change in photoresist linewidth Z with changes in exposure. The shaded area might represent the Z required to maintain aluminum linewidth specifications for a particular product. By selecting the intersection of each constant-exposure line with the center of the desired linewidth range, an optimal development time can be found for each exposure. The slopes of these relations describe the horizontal development rate of the overhang structure.

Lower exposures show a slower rate of change in linewidth. Since these linewidths are essentially functions of the total development process (time, concentration, temperature), one can see that the effect of minor changes in these process variables is significantly reduced at lower exposures. Thus, small day-to-day fluctuations in either exposure or development conditions, which routinely occur on a manufacturing line, can be accommodated (*i.e.*, the linewidths actually obtained remain within specification). In addition, there is increased flexibility allowed if lower exposures are used, since a desired overhang structure can be obtained over a larger range of development times. Shifting to lower exposures and longer development times was thus the first process enhancement we initiated. Another important conclusion is that the increasing rate of change of the resist linewidth with increasing exposure proves that, for the range of linewidths within which the manufacturing line must operate, the resist is partially exposed. The impact of this partial exposure was greater than expected.

Overhang

It is difficult to obtain reproduceable overhang structures at *any* exposure condition because both the foot and top must be simultaneously controlled by optimizing the soaking conditions for the particular development and exposure.

The overhang structure is produced in the unexposed portion of the photoresist. Figure 5(a) shows the overhang O as a function of development time for several exposure levels using a constant soaking time. Note that no positive overhang could be achieved with the highest exposure; the size of the overhang steadily increased with increasing development time for the lowest exposure. For the intermediate exposures, the overhang reached a maximum and then decreased with further development. These effects are the result of partial exposure of the remaining photoresist and development of the overhang itself from both top and bottom surfaces. From the decreasing overhang obtained with higher exposure and the effect of higher exposure on the development rate of Z, we conclude either that the partial exposure is greater at the top of the resist or that it affects the soaked layer more dramatically.

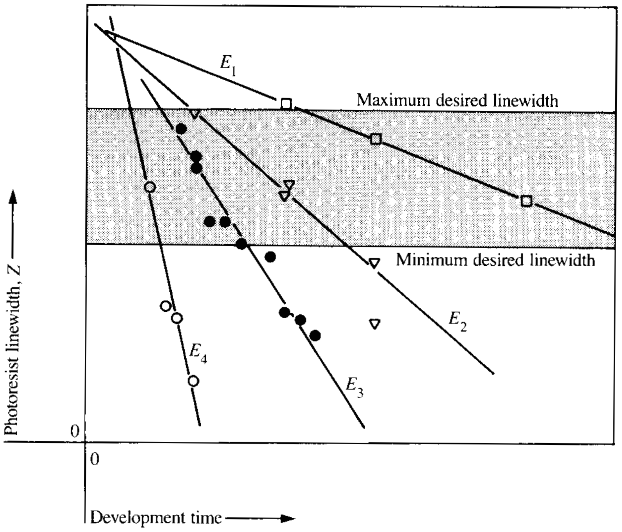

Figure 4 Lateral development rates in the unexposed soaked region. The linewidths are plotted as functions of the exposure E, where $E_1 < E_2 < E_3 < E_4$. The lines represent constant exposure. Notice the improved stability at lower exposure.

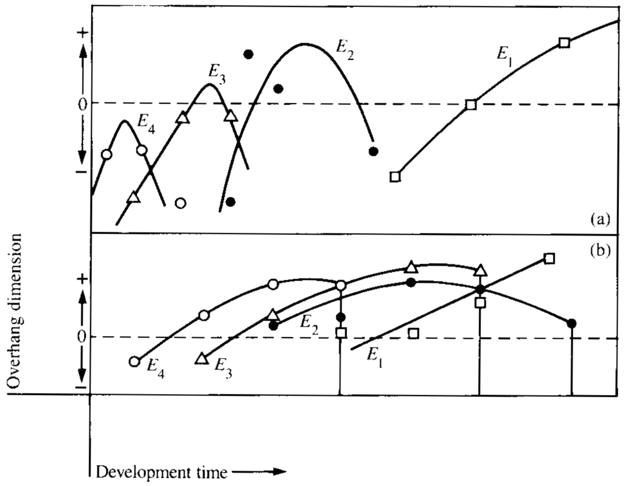

Figure 5 (a) Overhang *vs.* development time for a series of exposures E, where $E_1 < E_2 < E_3 < E_4$. These experiments were run under a constant soaking time. A positive overhang is indicated along the vertical axis as +, whereas a negative (no) overhang is denoted −. (b) Overhang *vs.* development time for a series of exposures E, where $E_1 < E_2 < E_3 < E_4$. These experiments were run using a constant baking temperature and soaking time. Vertical lines indicate points at which the structure collapses.

One further consideration involves the lateral development that occurs because of thinning of the overhang. This can influence both Z and O; see Fig. 6. In addition, widening of the parabola [see Fig. 5(a)] with reduced exposures causes a greater difference in the lateral development rates between the top and foot. Therefore, lower exposures produce more controllable overhang structures.

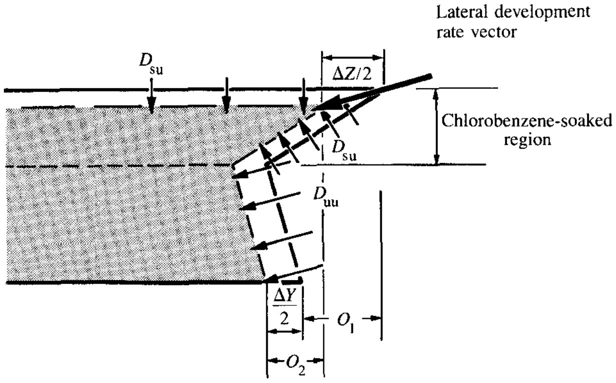

Figure 6 Degradation in the overhang due to development of the top of the structure from both top (D_{su} is the development rate in the soaked unexposed region) and bottom surfaces (D_{uu} is the development rate of the unsoaked unexposed resist). Note that if $D_{su} = D_{uu}/2$, $O_1 > O_2$ and $\Delta Z > \Delta Y$.

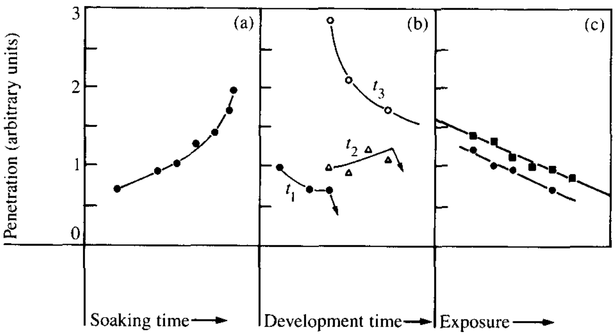

Figure 7 Penetration as a function of (a) soaking time, (b) development time (for different soaking times t, $t_1 < t_2 < t_3$), and (c) exposure. In (c) the lines refer to two completely different sets of processing parameters, in which the soaking times, baking temperatures, and development times all differ.

The overhang decreased when the soaked layer was thinned to the point where lateral development of the overhang proceeded faster than the development rate of the foot. This is due to development of the overhang from top and bottom surfaces. Figure 6 shows the example in which $D_{uu} = 2D_{su}$. For $D_{uu} > 2D_{su}$, further development consistently reduced the overhang.

The liftoff process must be arranged so that a positive overhang is always present. Adjustments for image-size control must be limited so that they do not destroy the overhang. Although post-development inspection with a microscope can be used to measure linewidths, it cannot be infallibly used to measure overhang since negative and positive overhangs cannot always be distinguished from one another. This overhang, however, can be easily measured using SEM images. Thus, any substantial proposed shift in process variables *must* have SEM verification that the proper overhang is present.

- *Height*

As both the development time and exposure increase, the structure height A decreases in a linear relationship. However, the shrinkage observed at higher exposures can be explained only by partial exposure of the "unexposed" photoresist. The height A is also affected by the soaking time; however, in order to fully understand these effects, we need to understand how penetration of the chlorobenzene into the resist is measured.

Soaking conditions

- *Penetration*

The penetration parameter, $(A - C)/A$, has been used to measure the extent of the soaked layer. It is obtained by measuring the height of the neck, as observed in SEM photographs, and assumes that the neck height is equivalent to the depth of chlorobenzene penetration. However, the shape of the neck is also influenced by exposure and development conditions. These processes obviously do not affect the chlorobenzene penetration, but they do influence the measurement of penetration through their effect on the position of the neck. Figures 7(a–c) show the relationships of the measured penetration to changes in the soaking, development, and exposure conditions. Although the penetration appears to increase rapidly with increases in the soaking time [Fig. 7(a)], such a relationship is unlikely for a diffusion-controlled process, as was shown in [5]. The data were obtained at a constant development time. For the longer soaking times, the liftoff profiles are actually underdeveloped, making the neck height appear to be less than it actually is. In Fig. 7(b) penetration appears to be decreasing with increasing development because overdevelopment of the structure thins the overhang, making the neck appear taller. In Fig. 7(c), increased exposures appear to cause decreases in the penetration because partial exposure increases the development rate of the overhang, making the neck appear taller. These effects show that penetration is not a useful measurement of the actual depth of chlorobenzene penetration. In addition, it cannot be used as a reliable means for controlling linewidths from day to day. When penetration is used as a measured parameter, all the processing steps must be tightly controlled.

Figure 7(c) also demonstrates the range of the chlorobenzene process. Not only are identical penetration measurements obtained for these very different processes, but all other structural features are identical. There are very different process windows for each exposure and for each of these processes. The optimal process is determined by plotting overhang and linewidth as functions of the development times, and then picking the process with the smallest rate of change.

Measuring the resist loss resulting from the soaking operation provides a measure of the influence of the chlorobenzene and eliminates the complications just discussed. The soaking process removes casting solvent and low-molecular-weight polymer. The loss of these materials can be tracked by measuring the changes in resist thickness. Resist loss *after soaking and rinsing in freon* [6] is used to monitor and control the chlorobenzene soaking process. Penetration measurements can then be correlated to resist loss (see discussion in the next section).

- *Linewidth*

Figure 8 shows how the photoresist linewidth Z is affected by development times for a series of soaking times. Longer soaking times produce thicker soaked films and lead to two separate effects on Z. First, the longer time required for development of the exposed regions delays the initial formation of the overhang. After this initial period, the unexposed soaked region is developed from both top and bottom surfaces, leading to a slower rate of change in Z for longer soaking times. The longer soaking times produce thicker overhangs, which are less sensitive to thinning by the developer.

- *Overhang*

As with the linewidth, the rate of change of the overhang is a function of both soaking and development processes (see Fig. 9). The soaking time also affects the foot structure by lengthening the time required to develop through the exposed soaked region. The development rates at the foot are completely independent of the soaking conditions. Therefore, a greater overhang can be created for long soaking times with long development times. The rate of change in structural features also is less sensitive to the development times at longer soaking conditions.

Figure 5(b) is a plot of overhang *vs.* development time for exposures similar to those used in Fig. 5(a). Longer soaking times reduce the sensitivity to exposure and development by producing thicker overhangs. Equivalent overhangs can now be created at higher exposure levels with deeper penetration. Note that the maximum overhang achieved in Fig. 5(b) corresponds to the best liftoff structure obtained in Fig. 5(a). The vertical lines indicate the points at which the structure collapses (neck width approaches zero).

- *Height*

The height A of the liftoff structure is increased by longer soaking times or deeper chlorobenzene penetration. This is surprising because 1) longer soaking times result in more resist thinning after soaking (see discussion in next section) and 2) the development rate D_{su} is not affected by soaking time, as shown by the constant slopes in Fig. 10. Therefore, we suspect that the height A must be influenced by dissolution by the developer of material from the *unsoaked* region of the structure. The longer soaking times, *i.e.*, deeper penetrations, result in smaller unsoaked resist thicknesses being exposed to the developer. Hence, the surface area of photoresist that is susceptible to removal is decreased.

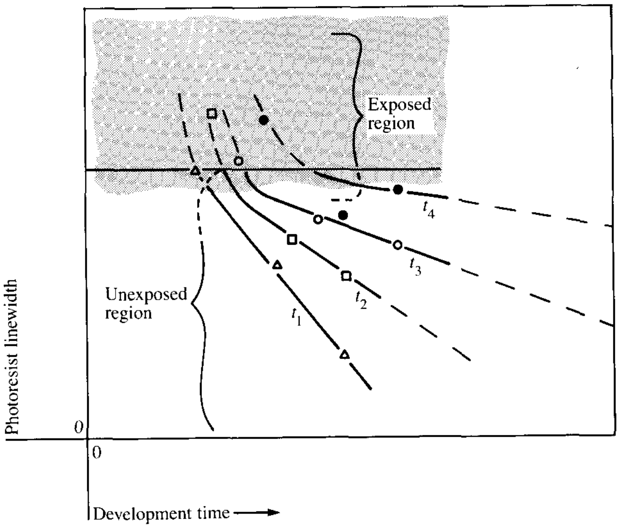

Figure 8 Photoresist linewidth *vs.* development time for a series of soaking times t, where $t_1 < t_2 < t_3 < t_4$.

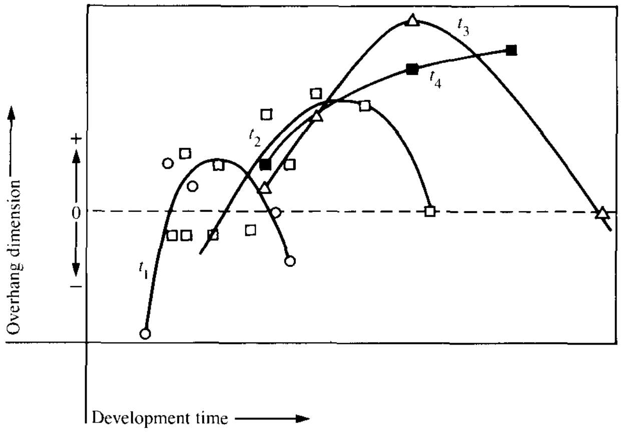

Figure 9 The overhang *vs.* development for a series of soaking times t, where $t_1 < t_2 < t_3 < t_4$. These experiments were run under constant exposure and baking temperature.

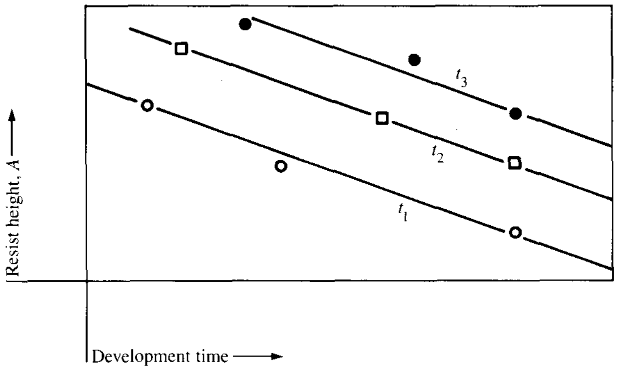

Figure 10 Resist height A *vs.* development time for a series of soaking times t, where $t_1 < t_2 < t_3$.

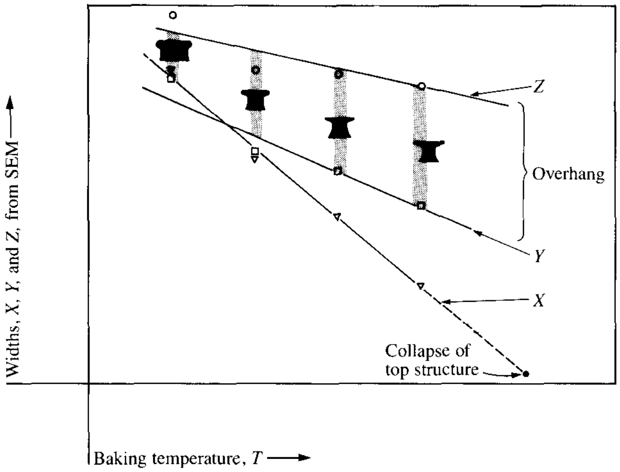

Figure 11 Top (Z), foot (Y), and neck (X) widths as functions of the baking temperature T, for one set of optimized process parameters.

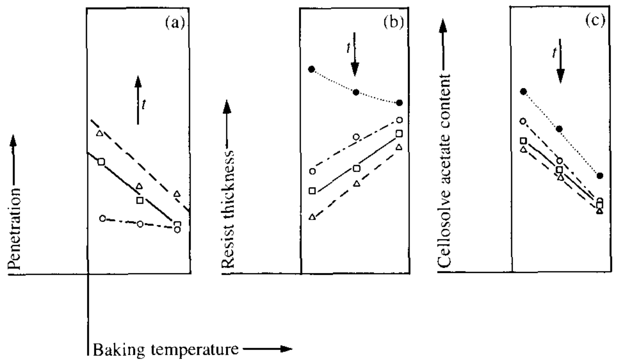

Figure 12 (a) Penetration, (b) resist thickness, and (c) ®Cellosolve acetate content as functions of the baking temperature for a series of soaking times t, where $t_0 = 0$ (●) $< t_1$ (○) $< t_2$ (□) $< t_3$ (△).

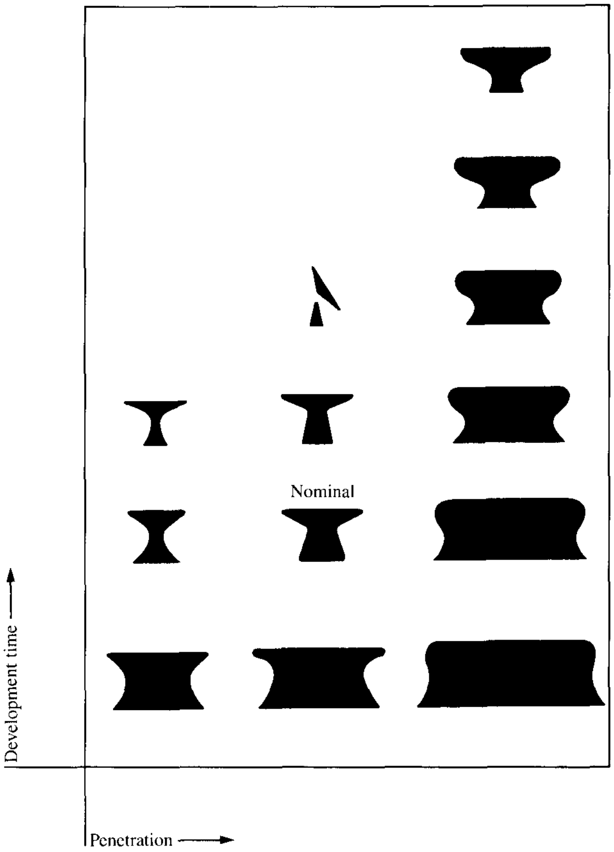

Figure 13 Changes in the overhang structure as a function of the development time and the penetration for a constant exposure. Shallow penetrations (first three structures on the left) do not develop an overhang. Penetrations greater than about 35% (structures on right) produce structures with inadequate neck height for constant liftability.

Baking conditions

Variation of the photoresist application baking temperature or time produces the greatest rate of change in the overhang structure, as seen in Fig. 11. Baking controls the overhang structure through its influence on the chlorobenzene soak. Baking influences the soaking operation by controlling the amount of casting solvent left in the photoresist. The diffusion rate of chlorobenzene into the resist is a function of the casting solvent present. Higher baking temperatures or longer baking times result in lower solvent contents and lower chlorobenzene diffusion rates, and require longer soaking times to produce an equivalent structure. Figures 12(a–c) show that measurements of penetration, resist loss, and ®Cellosolve acetate [7] content, as functions of the baking temperature, all yield identical results. Further, the figures show how each parameter varies with soaking time and the influence of the baking temperature on each soaking condition. Increased baking temperatures normalized the soaking effect for all three parameters

Just as soaking can be used to normalize exposure and development influences, higher baking temperatures can be used to normalize the influence of soaking parameters on process stability. Even with tightly controlled experimental conditions, the largest scatter of data is obtained for measurements of penetration. Measuring resist thickness before and after soaking yields a parameter that predicts the effect on the liftoff structure of the *combined* baking and soaking processes. Lower baking temperatures (or longer soaking times) provide resist films that require longer development to penetrate the exposed soaked region. Therefore, after development the resist overhang structure is taller (Fig. 10). Correlation of the penetration measurements with resist losses provides the capability for ensuring more valid measurements of the chlorobenzene penetration and for separating the baking and soaking processes from the effects of exposure and development.

Summary

The data in this paper are summarized in Figs. 13 and 14, which show the relationships among exposure, development, and penetration, and their effects on the overhang structure. Penetration is used to represent the combined effects of baking and soaking. Figure 13 illustrates how identical structures can be created by matching proper development times with exposure; however, the rate of change, or the ability to control processes, is significantly better at lower exposures. Figure 14 shows that shallow penetration produces rapid changes in the resist structure similar to those obtained at high exposures. Too little a penetration creates an unstable structure with insufficient overhang. Too great a penetration produces structures with poor liftability because of the reduced neck height. A manufacturing process should be optimized towards low exposures, deeper penetration, and high baking temperatures, thus providing a process that is less sensitive to development time.

The process variables in the chlorobenzene liftoff process can be controlled in a high-volume production line by monitoring the linewidth, overhang, and height. A combination of computer-monitored processes, image-size measurements, and SEMs of the structure can be used to control this single-step liftoff process.

Acknowledgments

We thank the following coworkers: W. Motsiff, M. MacIntyre, and R. Halverson for analytical work which defined the chemical mechanisms; R. Danyew for his SEM micrographs; M. Hannon and D. Slack for their support and coordination of all experiments; and M. Haller and M. Hampe for their technical expertise and initial support in the experimental designs.

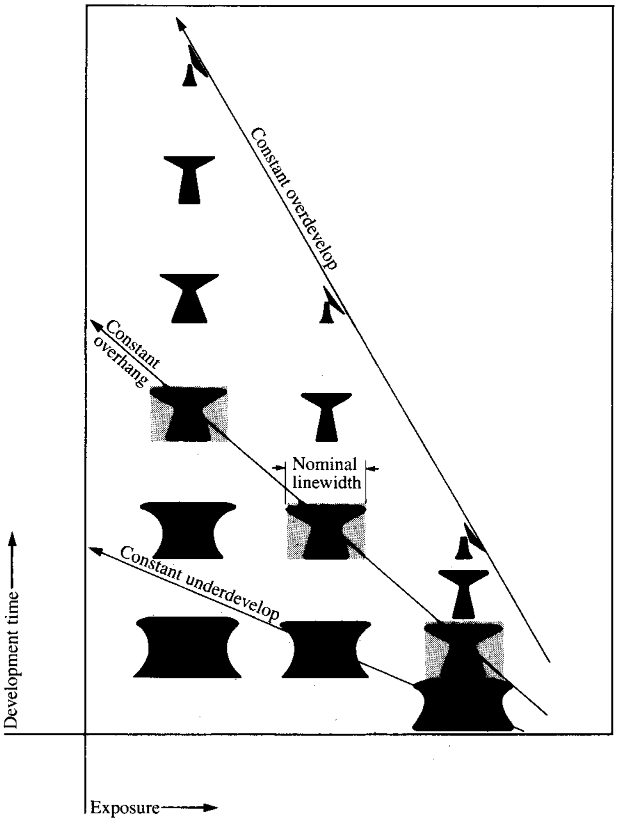

Figure 14 Changes in the overhang structure as a function of development time and exposure for a constant value of penetration. Lines of constant degree of development show identical overhang structures. Lower exposures provide improved stability in the structure parameters.

References and notes

1. B. J. Canavello, M. Hatzakis, and J. M. Shaw, "Single-Step Optical Lift-Off Process," *IBM J. Res. Develop.* **24,** 452–460 (1980); "Process for Obtaining Undercutting of Photoresist to Facilitate Lift-Off," *IBM Tech. Disclosure Bull.* **19,** 4048 (1977); "Method for Modifying the Develop Profile of Photoresists," U.S. Patent No. 4,212,935 (filed 2/24/78, issued 7/15/80).
2. Richard A. Larsen, "A Silicon and Aluminum Dynamic Memory Technology," *IBM J. Res. Develop.* **24,** 268–282 (1980).
3. Zane Apgar, "Control Systems for Memory Manufacturing," *Proc. Autofact West* **2** (Society of Manufacturing Engineers, Dearborn, MI), 615–634 (1980).
4. ®AZ is a registered trademark of the Azoplate Division of the American Hoechst Corp., Somerville, NJ 08876; their licensed distributor is the Shipley Co., Newton, MA.
5. R. M. Halverson, M. W. MacIntyre, and W. T. Motsiff, "The Mechanism of Single-Step Liftoff with Chlorobenzene in a Diazo-Type Resist," *IBM J. Res. Develop.* **26,** 590–595 (1982, this issue).
6. The resist film swells during chlorobenzene soaking but ultimately shrinks when the chlorobenzene is removed by the freon rinse.
7. ®Cellosolve acetate is a product of Union Carbide Co., New York, N.Y.

Received August 12, 1981; revised March 19, 1982

George G. Collins *IBM Japan Ltd., 800 Ohaza Ichimiyake, Yasu-Machi, Yasu-gun, Shiga-ken 520-23, Japan.* Mr. Collins first joined IBM's Components Division in 1964 as a student, obtaining an academic leave of absence one year later to complete a degree in chemical engineering at the University of Delaware, which he received in 1969. Returning to Burlington, Vermont, in quality and manufacturing engineering, he concentrated on process control systems, for which he received an IBM Outstanding Contribution Award in 1971. Four years as a marketing representative in the Data Processing and General Systems Divisions selling process control systems earned him a Southern Region Award in 1973 and the General Systems Division Award in 1974. From 1975 to 1980, Mr. Collins was involved in SAMOS, focusing on process manufacturing engineering, oxidation, photolithography and CVD/LPCVD; for his efforts he received the IBM President's Award in 1980. Currently Mr. Collins is on assignment in Japan as an advisor.

Cary W. Halsted *IBM General Technology Division, Burlington facility, Essex Junction, Vermont 05452.* Prior to joining IBM in 1971, Mr. Halsted worked for two summers at Burlington. Presently he is working in the areas of SAMOS manufacturing engineering photo, hot processing, and semiconductor characterization. He received his B.S. in chemical engineering in 1969 from New York University, Washington Heights, and his M.S. in chemical engineering in 1970 from the University of Michigan, Ann Arbor. Mr. Halsted is a member of the Electrochemical Society.