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# The Mechanism of Single-Step Liftoff with Chlorobenzene in a Diazo-Type Resist

*The mechanism of the chlorobenzene single-step liftoff process is defined. The chlorobenzene penetrates to some depth into the resist film during the soaking cycle, extracting residual casting solvent and low-molecular-weight resin species. The chlorobenzene is subsequently removed by a rinse cycle. The penetrated layer of resist develops at a slower rate than the underlying bulk resist, producing the liftoff structure.*

## Introduction

High-density integrated circuit memory products require utilization of a liftoff metallization technique in order to meet the design ground rules for the wiring layers. The liftoff concept utilizes the formation of a stencil pattern on a wafer surface, which is followed by blanket metallization over the stencil. The stencil and the metal it supports are subsequently removed from the wafer by use of an appropriate solvent, leaving the metal wiring pattern on the wafer.

M. Hatzakis *et al.* [1] have observed that immersion of ®AZ-1350J [2] in chlorobenzene after post-application baking but prior to development alters the cross-sectional profile of the developed resist images. This chlorobenzene treatment reduces the dissolution rate of the outermost resist surface in aqueous alkali developer solutions, but does not affect the dissolution rate of the underlying bulk resist. The resultant differential development yields cross-sectional resist profiles that are characterized by a maximum width at the top, outermost surface. These undercut profiles are necessary for the successful use of liftoff metallization techniques in the manufacture of integrated circuit devices. This paper presents the mechanism of this chlorobenzene single-step liftoff process. Note that the companion paper in this issue by Collins and Halsted [3] discusses details of the process control of this technique in a manufacturing environment.

## Preliminary studies

The chlorobenzene effect must result from chemical and/or physical interaction between chlorobenzene and one or more of the components of positive photoresist films. The ®AZ-1350J LOR (liftoff resist), abbreviated JLOR, consists of a photoactive orthonapthoquinone diazide and a phenolic resin composite (J resin plus a phenolic resin additive) dissolved in a solvent system consisting of ®Cellosolve [4] acetate, butyl acetate, and xylene. Since no obvious chemical reactions can occur between chlorobenzene and any of these components, physical extraction of one or more of them appeared to be the most probable interaction.

Extraction of the resist components can only occur if they are soluble in chlorobenzene; thus, solubility studies were performed to eliminate from consideration any impossible extractions. The three components of the casting solvent were completely soluble in chlorobenzene, whereas the photoactive compound was soluble to the extent of three weight percent. Only the low-molecular-weight fractions of the resin composite were soluble in chlorobenzene, indicating that extraction of all three component systems was possible. However, extraction of any residual casting solvent is most probable. The following studies were performed to better define the role of these three possible interactions in the formation of the chlorobenzene effect.

## Solvent studies

The study of the residual casting solvent in resist films and their interaction with chlorobenzene required the development of an analytical technique for quantitatively determining the solvent content of the resist films. This technique

involved the complete dissolution of the resist film in high-purity N-methyl-2-pyrrolidinone and subsequent gas chromatographic analysis of the solution using a 10% Carbowax 20M column [5]. An initial precision study of five consecutive resist films after resist application and drying yielded an average ®Cellosolve acetate content of 1.89 ± 0.03 micromoles. The ®Cellosolve acetate was the only residual casting solvent present after the post-application drying.

The ®Cellosolve acetate content of the resist films was then studied as a function of the post-application-baking temperature and time. At a constant baking time, an almost linear decrease in ®Cellosolve acetate was observed as the post-application-baking temperature was increased. A nonlinear decrease in the residual ®Cellosolve acetate content was seen as the post-application-baking time was increased at a constant baking temperature. These studies demonstrated that the residual ®Cellosolve acetate content of the resist films is clearly a function of both the post-application-baking time and the temperature [6].

The role that the residual ®Cellosolve acetate content plays in controlling the amount of chlorobenzene picked up by resist films is illustrated for a typical case in Fig. 1. The greater the ®Cellosolve acetate content of the resist film, the greater the amount of chlorobenzene absorbed into the film during the soak. This occurs due to the dramatic effect of the solvent content in a polymer matrix on the diffusion coefficient of a solvent in that matrix [7]. As the amount of residual ®Cellosolve acetate in the resist films increases, the apparent diffusion coefficient for chlorobenzene into the resist film increases, thereby increasing the amount of the chlorobenzene absorbed for a given soaking time.

In order to remove surface chlorobenzene before further processing, a freon vapor rinsing and drying operation is performed after the chlorobenzene soak [8]. During these studies, this operation was found to have an effect on the chlorobenzene content of the resist films. If the films were simply dried by blowing nitrogen over them, a significant amount of chlorobenzene was found in the films. However, after an identical soak followed by freon rinsing and drying, the level of chlorobenzene in the resist films was barely detectable. The effect of this residual chlorobenzene on the development rate of the soaked resist film is discussed at the end of this section.

Further quantitative studies indicated that as the chlorobenzene content of the soaked resist films increased, the ®Cellosolve acetate content decreased. The longer the soak, the greater the chlorobenzene absorption and the greater the loss of ®Cellosolve acetate. This loss occurs by diffusion of the ®Cellosolve acetate out of the resist film. As the chlorobenzene content of the film increased, the apparent diffusion

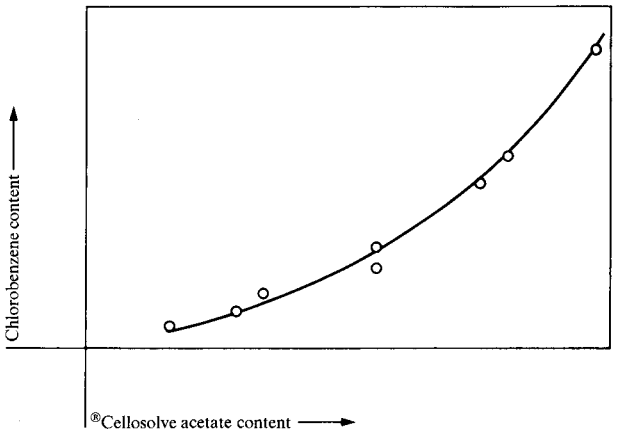


**Figure 1** The chlorobenzene content of soaked JLOR films as a function of ®Cellosolve acetate content after a typical post-application bake, chlorobenzene soak, and nitrogen blow-dry cycle.

coefficient for ®Cellosolve acetate in the film increased. This increase allows the ®Cellosolve acetate to rapidly diffuse out of the film into the ®Cellosolve-acetate-free chlorobenzene. The data indicated non-Fickian behavior of the chlorobenzene diffusion and Fickian behavior for the ®Cellosolve acetate diffusion. The apparent non-Fickian behavior of the chlorobenzene diffusion is expected for solvent diffusions occurring below the glass transition temperature of the polymer [9]. The apparent Fickian behavior of the ®Cellosolve acetate diffusion, however, is surprising; it may be due to diffusion occurring *after* absorption of chlorobenzene, and to consequent solvation of the polymer matrix. Addition of other acetate or ester cosolvents would also be expected to alter the diffusion kinetics and, thereby, the chlorobenzene content [10, 11]. This has been verified for n-butyl acetate.

A study was made to compare the penetration of the chlorobenzene effect (by observation of the overhang thickness) and loss of ®Cellosolve acetate from resist films for different soaking times. The percentage penetration was calculated from measurements of scanning electron microscope (SEM) photographs of the cross-sectional profiles of developed liftoff resist images, after correcting for any resist losses that occurred during the soaking and development steps. The two percentages consistently correlated for different soaking times, indicating a direct relationship between the loss of ®Cellosolve acetate and the depth of penetration of the chlorobenzene.

In order to study this relationship, the ®Cellosolve acetate content, the chlorobenzene content, and the dissolution rate of unsoaked and soaked resist films were profiled as a function of resist thickness. The soaked films were either thoroughly rinsed and dried in freon or blown dry with

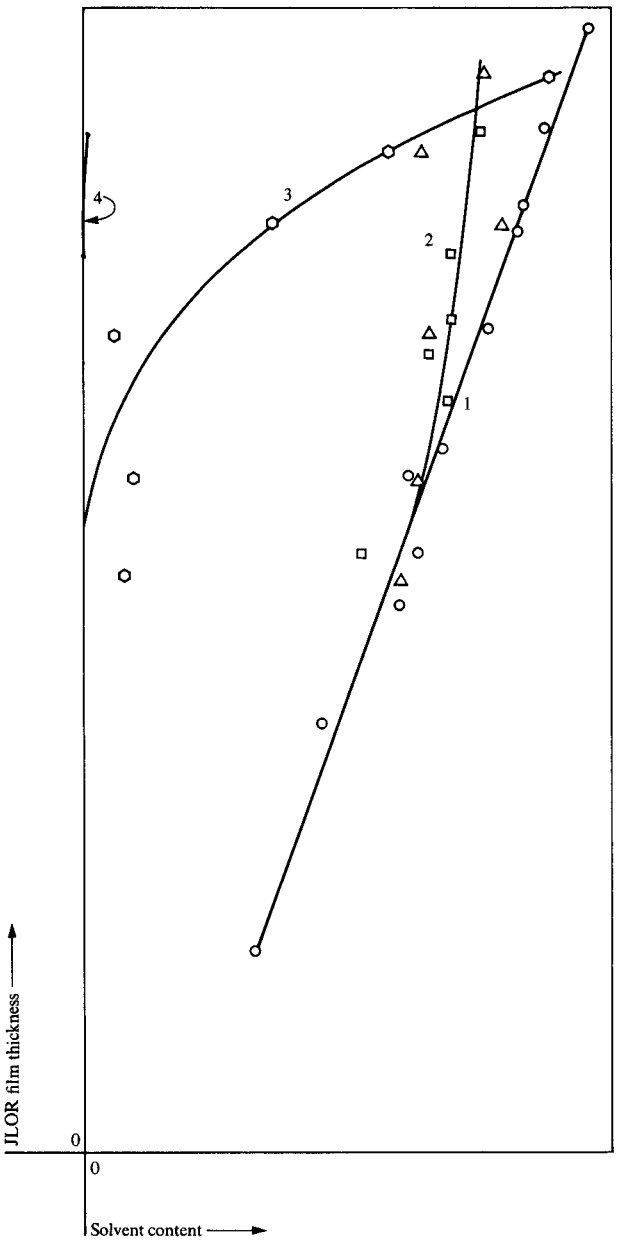


**Figure 2** The solvent content of chlorobenzene-soaked and unsoaked JLOR films as a function of film thickness. Curve 1: No soaking; ®Cellosolve acetate content. Curve 2: Typical soaking time, nitrogen blow dry; ®Cellosolve acetate content (△) and typical soaking time, freon rinsing and drying step; ®Cellosolve acetate content (□). Curve 3: Typical soaking time, nitrogen blow dry; chlorobenzene content. Curve 4: Typical soaking time, freon rinsing and drying step; chlorobenzene content.

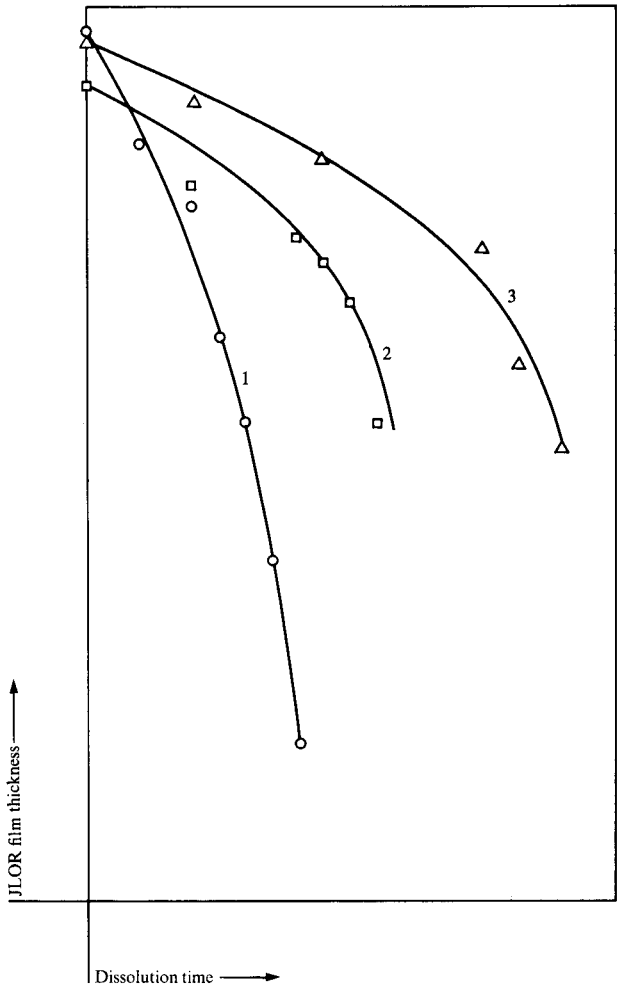


**Figure 3** The thickness of unsoaked (Curve 1) and chlorobenzene-soaked (Curves 2 and 3) JLOR films as a function of dissolution time. For the soaked films, Curve 2 is for the freon-rinsed-and-dried film and Curve 3 is for the nitrogen-blown-dry film. All films underwent a typical post-resist-application bake, and development was in KOH solution.

nitrogen. This profiling was accomplished by first determining the thickness of a set of resist films, dissolving them for a range of times in an aqueous KOH solution, remeasuring their thicknesses, and then quantitatively determining their solvent contents. These data were used to plot the profile curves presented in Figs. 2 and 3. The unsoaked films had a uniform distribution of ®Cellosolve acetate and a slowly accelerating dissolution rate. The chlorobenzene-soaked and freon-rinsed-and-dried films had a significantly reduced ®Cellosolve acetate content, a barely detectable chlorobenzene content, and a significantly reduced dissolution rate (by $\approx 6\times$) down to a transition zone. Below this transition zone, the bulk resist had a uniform distribution of ®Cellosolve acetate and the normal dissolution rate of an unsoaked film. The soaked and nitrogen-dried films also had a reduced amount of ®Cellosolve acetate, but contained significant amounts of chlorobenzene and a further reduced dissolution rate (by $\approx 8\times$) down to the transition zone.

These data indicate that during the soaking process the chlorobenzene diffuses into the resist film, allowing the ®Cellosolve acetate to diffuse out. An efficient freon rinsing and drying step removes the chlorobenzene, leaving a layer of solvent-deficient resist that develops slower than the bulk resist (by $\approx 6\times$). If this rinsing and drying step is eliminated, the chlorobenzene remains in the resist surface layer, further reducing its dissolution rate (by $\approx 8\times$).

## Resin studies

The extraction of low-molecular-weight species from phenolic resins by chlorobenzene has been demonstrated [1(a)]. Our investigation required a technique which would elucidate the actual changes occurring to the resin in resist films during chlorobenzene soaking. The technique developed consisted of dissolution of chlorobenzene-soaked and unsoaked blanket resist films in high-purity tetrahydrofuran and subsequent gel permeation chromatography (using a series of decreasing-pore-size Styragel columns) to determine the relative molecular weight distributions of the resin in these solutions. Additionally, dissolution rates of resin films cast with both chlorobenzene-washed and unwashed resins were determined as functions of the amount of residual casting solvent (®Cellosolve acetate).

Soaking was found to reduce the amount of low-molecular-weight resin in the resist. The magnitude of this decrease increases with increasing soaking time, as does the magnitude of the loss of ®Cellosolve acetate and the observed depth of penetration of the chlorobenzene into the resist film. This correlation is displayed in Fig. 4. It is evident that immersion of resist films in chlorobenzene produces films whose outermost regions are deficient in both ®Cellosolve acetate and low-molecular-weight resin species.

Since both of these effects should depress the dissolution rates of phenolic resins [1(b), 12], we investigated the relative magnitudes of reduction in these dissolution rates. The dissolution character of chlorobenzene-washed and unwashed phenolic resins similar to those used in ®AZ-1350J and JLOR was explored. The chlorobenzene washing procedure we used consisted of pulverizing the resin, slowly adding this powder to the chlorobenzene with agitation, and continuing agitation for an extended period of time. The washed powder was then filtered and dried in a vacuum oven.

Figure 5 shows the results of these studies. They are similar to Ouano's [13], with all systems displaying decreased dissolution rates as residual casting solvent is reduced. This figure also shows that chlorobenzene washing decreases the dissolution rates of all the resin systems. Interestingly, the solubility rates of ®AZ-1350J and similar-type resins show greater sensitivity to solvent content and washing than the JLOR-type composite.

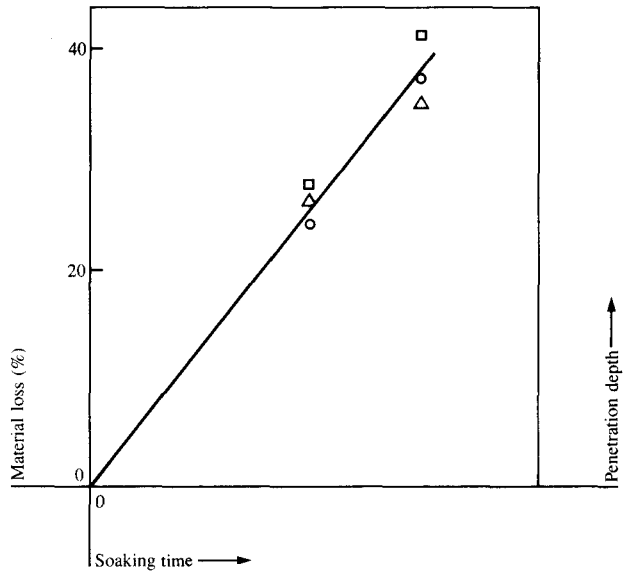


**Figure 4** Correlations between the loss of low-molecular-weight resin (△), ®Cellosolve acetate (○) and the penetration depth of the chlorobenzene into the JLOR films (□) with soaking time. All samples saw a typical post-application bake.

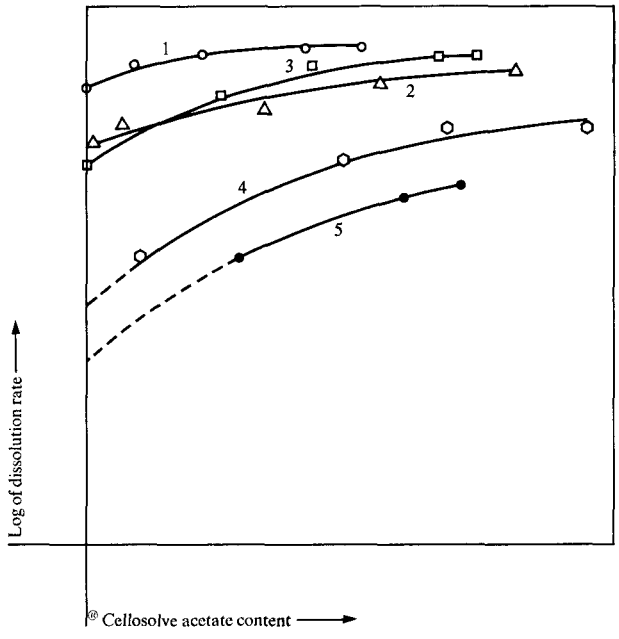


**Figure 5** Resin film dissolution rates (KOH) as a function of the ®Cellosolve acetate content: unwashed (Curve 1) and chlorobenzene-washed (Curve 2) JLOR-type resin composites; unwashed (Curve 3) and chlorobenzene-washed (Curve 4) J-type resins; and JLOR (Curve 5).

The resin investigations have shown that chlorobenzene soaking removes low-molecular-weight species from the resin. The amount of low-molecular-weight material lost corre-

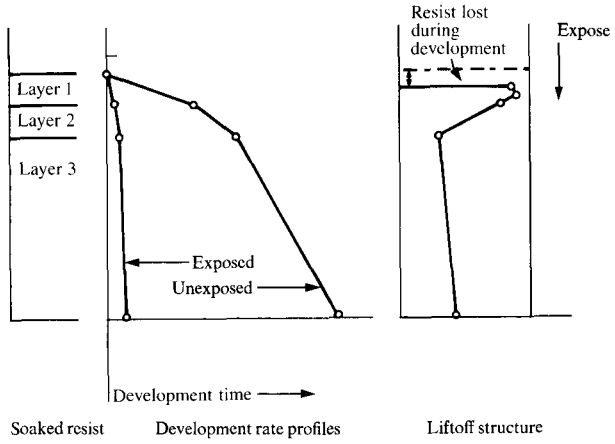


**Figure 6** A schematic illustration of a chlorobenzene-soaked JLOR film, its development rate profiles, and the consequent liftoff structure after development.

lates with the amount of ®Cellosolve acetate lost and with the depth to which the chlorobenzene has penetrated into the film. Removal of low-molecular-weight species and ®Cellosolve acetate reduces the resin dissolution rate by similar magnitudes.

## Studies of the photoactive compound (PAC)

The effect of soaking in chlorobenzene on the PAC present in resist films was also investigated. Electron spectroscopy for chemical analysis (ESCA) studies of the surface of chlorobenzene-soaked and unsoaked films revealed that soaking removed the PAC [13]. However, angular rotational profiling of soaked films by ESCA showed the PAC content rapidly increasing down to the approximate 10-nm depth of its measurement [13]. The curves for the dissolution rates of JLOR and the JLOR-type composite resin in Fig. 5 show that removal of PAC to any significant depth into the resist film should dramatically increase the dissolution rate of that layer of resist (by $\approx 25\times$). Since we had measured a dissolution rate decrease (by $\approx 6\times$) in the chlorobenzene-penetrated portion of JLOR films, it was concluded that the PAC removal during soak was minimal and played no significant role in the chlorobenzene effect.

## Summary of the mechanism

When the results of the preceding studies of the chlorobenzene interaction with the components of resist films are combined, the mechanism of the chlorobenzene liftoff effect becomes evident. A schematic illustration of a chlorobenzene-soaked resist film, its dissolution rate profile, and the consequent liftoff structure after development is shown in Fig. 6.

For the purpose of this illustration, the soaked resist film is considered to be comprised of three layers, each having a distinct dissolution rate. The outer, most thoroughly chlorobenzene-modified layer, has the lowest rate, while the resist adjacent to the wafer has the highest rate. It is assumed that the resist is exposed using a mask of high image/edge contrast, and that no scattering or reflection of light occurs in the film. Development is assumed to be isotropic.

An outline of the mechanism of the chlorobenzene single-step liftoff process described in this paper is as follows:

1. Chlorobenzene diffuses into the resist film, swelling it and forming a gel to the depth of the diffusion. The rate of this diffusion is controlled by the ®Cellosolve acetate content of the resist film and by the impurity content of the chlorobenzene.
2. ®Cellosolve acetate and low-molecular-weight resin species diffuse out through the chlorobenzene-resist gel, leaving a layer in the resist that is deficient in ®Cellosolve acetate and low-molecular-weight resin. This layer extends to the depth of chlorobenzene diffusion. Some surface PAC also diffuses out of this gel.
3. The freon rinsing and drying step removes chlorobenzene from the resist, leaving a dry layer of resist to the depth of the chlorobenzene diffusion. The dissolution rate of the dry layer is less than that of the bulk resist. If residual chlorobenzene remains in this surface layer because of inadequate rinsing, its dissolution rate is further reduced.
4. This differential dissolution between the penetrated layer and the bulk resist causes formation of the liftoff profile during resist development. The amount of overdevelopment and the ratio of the rates determine the specific profile shape; see Ref. [3].

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