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SPRAY PHOTORESIST DEVELOPMENT
ON MULTIPLE HYBRID MICROCIRCUIT
SUBSTRATES

PDO 6984726, Topical Report

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Published May 1975

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SPRAY PHOTORESIST DEVELOPMENT ON MULTIPLE HYBRID MICROCIRCUIT SUBSTRATES

BDX-613-1148

May 1975

Prepared by L. E. Schantz, D/842, under PDO 6984726

This investigation revealed that spray development of Shipley AZ1350J photoresist on 95- by 114-millimeter substrates will maintain a line-width deviation less than ± 20 microinches ($\pm 0.5 \mu\text{m}$) on 5-mil ($127 \mu\text{m}$) circuit paths. The overall photolithography process is controlled to allow only a ± 3 -percent line-width change on 5-mil paths.

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SUMMARY

Spray development of photoresist images for HMC production was investigated as a part of *Multiple Hybrid Microcircuit Processing* (PDO 6984726) to reduce the cost of HMC photolithographic processing, increase capacity, and improve process control. This study of spray developing was conducted as a result of a previous development, in which the process-control advantages of spray development were recognized. A production model spray developer which eventually would be placed in production to save manpower and equipment costs was characterized.

A reduction in image developing costs and an increase in substrate capacity resulted from decreasing the time required to develop the resist-coated substrates. Previous manual developing times were 25 to 30 seconds per substrate, with a capacity of approximately five substrates per minute. Spray developing times are about 15 seconds per substrate, with a practical capacity of approximately 10 substrates per minute. Although the time required to spray process is initially only half that of the manual immersion-developing procedure, developing solution depletion during spray processing increases the developing time required. However, the capacity for most applications is essentially constant at about 500 substrates each hour.

A developing solution concentration monitoring and control method was established by Materials Engineering. This method (determining the spectral absorption by use of a colorimeter) worked very well for immersion developing, but failed to identify the solution depletion mechanism when used for spray developing. The developing solution appears to be depleted by absorption of oxygen or carbon dioxide from the air during spraying, although this has not been proven. An alkalinity test also was developed, but proved cumbersome for production use. An image-quality test was used to determine the solution life in terms of the number of days it will successfully develop the resist image with acceptable dimensional control. This information was used to propose an operational production approach for the developing system in terms of dimensional control of the resist image.

The developing time required for zero line-width deviation increases as the solution depletes. Therefore, by decreasing the conveyor speed as the solution depletes, the developing action can be held relatively constant, and the deviation on the line width can be minimized. If the conveyor speed is adjusted so that the developed image always appears at approximately the same location (or developing point) in the developing chamber regardless of the degree of developer depletion, the deviation can be held relatively constant. If the developing point is held at near three-fourths of the distance through the chamber, the line-width deviation will be near zero.

The effects of spray pressure and solution temperature were less than that produced by developing time. However, maximum spray pressure should be used, and the solution should be held at room temperature.

Facility considerations included adequate venting of fumes and containment of spills. Nitrogen purging of the developing chamber is needed to minimize contact of the developing solution with air.

Since commercial spraying equipment is inefficient in the use of solution, requires excessive floor space, and does not provide suitable substrate loading features, special Bendix designed and fabricated spray development equipment is recommended.

DISCUSSION

SCOPE AND PURPOSE

The spray photoresist development used for hybrid microcircuit fabrication was characterized to provide an improved and more consistent developing process, and as a part of an overall cost effective photolithography process. This work was to determine the boundary conditions for using spray processing equipment, investigate and resolve technical problems encountered during the study, and transfer the technology to Process Engineering for production use. The technology included the physical limits of the process parameters which would provide acceptable products. Material considerations included devising methods for monitoring the developing solution life and the depletion point. Recommendations of methods for production use and facilities considerations also were transferred to Process Engineering.

PRIOR WORK

There had been no previous work on large system HMC spray developers. However, during a previous development effort, certain applications of manual spray development provided better results than immersion development. The advantages of spray development were recognized at that time and were recommended for future investigation. The spray techniques used during the previous work were manual, with only single use of the developing solution. That method was not well suited for large scale production. Although an automatic spray developer with a recirculating solution reservoir was recommended, sufficient knowledge was not available to completely specify a spray processor which eventually would be used for production.

During the initial planning for the multiple hybrid microcircuit processing project, it was recommended that a laboratory version of a spray developer be designed and built to investigate large-scale spray developing. The information obtained would then be used by Process Engineering to specify a production model. However, due to limited manpower availability, the increased emphasis on moving multiple HMC processing into production and the relatively low cost of a production system, a commercial spray developer was procured for this development work and eventual transfer to production.

ACTIVITY

General

Previous process development work established that spray photoresist development produces results superior to immersion processing. Spray developing provides the following advantages:

- Faster developing time (increased production capacity);
- Increased line width resolution (permits smaller geometries);
- Improved line edge quality;
- More consistent process control (ensures repeatable HMC electrical characteristics); and,
- Better uniformity of developing action across large substrate surfaces (ensures consistent HMC electrical characteristics).

Because of these advantages, spray developing of photoresists for HMC fabrication was recommended as a production process.

A DEA Model 120 Jet-Spray was purchased for process development, believing that use of the same machine for subsequent production would save time, manpower, and cost. This philosophy worked well; however, unforeseen technical difficulties discovered during the characterization study negated some of the advantages. The danger of committing capital equipment funds to processing equipment when the supporting technology is not well understood is obvious. However, the cost of the production model was sufficiently low to be competitive with design and development of a laboratory model. Therefore, both time and money were saved by characterizing the machine and the spray process at the same time.

Machine Description

The DEA Jet-Spray-120 shown in Figure 1 is a horizontal, conveyORIZED spray processor quite similar to those used for etching printed circuit boards. The developing solution is sprayed from manifolds either above or below the conveyor, thus allowing images to be developed on the top or bottom of the substrate or on both sides simultaneously. The solution is recirculated from a 12- to 18-gallon reservoir. The developing chamber is followed by separate chambers for a deionized water rinse and nitrogen gas drying. The developer exit port was designed to mate with a companion chromium/gold etcher; however, the characterization approach did not exercise this option.

Figure 1. DEA-120 Spray Developer

The controls shown in Figure 2 are generally self-explanatory. Although there is a set-point temperature controller and a light that indicates a cooling cycle, there are no cooling coils. The machine is capable of heating the solution, but the solution is normally at room temperature. Under recommended operating conditions there is no temperature rise in the solution, but under continuous operation, there is a transfer of heat from the pumps to the solution reservoir. The other control functions of Figure 2 are as follows:

- *Pump 1* enables the Pump-1 motor and starts the spray to the bottom side of the substrate.

Figure 2. DEA-120 Control Panel

- *Pump 2* enables the Pump-2 motor and starts the spray to the top side of the substrate.
- *Heat* enables the heater to respond to the set-point controller. The temperature indicator on the set-point controller is operative at all times when the system power is on.
- *Conveyor* turns on the conveyor drive motor.
- *Air* turns on the nitrogen-gas drying knives.
- *Conveyor Speed* (10-turn potentiometer) adjusts the speed of the conveyor track.
- *Fast Exit* is a momentary switch that runs the conveyor at maximum speed while it is held on.
- *Alarm Stop* kills power to entire system when pressed.
- *Power On* provides electrical power to the system when pressed.

A ball valve between the pump and the manifold containing the spray nozzles provides simultaneous adjustment of the spray pressure and solution flow rate. Gages indicate the pressure in each manifold and the average flow rate in gallons per minute. The gages measure pressure, and the indicated flow rate is the sum of the average flow rates for each spray nozzle at the measured nozzle pressure. (The nozzle pressure is assumed to be the same as the manifold pressure.) For maximum uniformity of the solution spray and optimum developing uniformity across the entire chamber, the spray nozzles must be operated near the maximum pump pressure (with the ball valve completely open).

Sprayer Capacity

The developer capacity in substrates per hour is a function of the conveyor speed and the number of substrates abreast of each other on the conveyor. Since the conveyor is 20 inches (0.5 m) wide, it could theoretically accommodate three 3-3/4 by 4-1/2-inch (95 by 114 mm) substrates abreast; however, practical considerations of loading, substrate interaction, and spray uniformity limit the conveyor capacity at two such substrates abreast. In fact, no two substrates will be abreast of each other unless they are loaded simultaneously. Because substrates are loaded one at a time, the second substrate will most likely be somewhat behind the first on the conveyor. The third substrate will follow the first. For this reason, the capacity is predominantly governed by the conveyor speed at low speeds and by swiftness of loading the substrates at higher speeds.

Figure 3 shows the conveyor speed in inches per second as a function of the speed controller setting. The conveyor speed is not an independent variable, but is determined by the required photoresist developing time, as discussed later. However, once the developing time is determined and the appropriate conveyor speed is determined, Table 1 may be used to approximate the system capacity.

Figure 3. Conveyor Speed Versus Machine Control Setting

Table 1 shows that the conveyor speed is not the factor that limits capacity. The conveyor is expected to outpace the operator who manually loads the system at all speed settings greater than 20. Therefore, the ultimate capacity is limited by loading and unloading.

The amount of time each substrate is in the developing chamber and in the system is fixed by the conveyor speed, as shown in Figures 4 and 5. Each substrate is developed for the same amount of time, thus affording a consistent processing approach that is nearly free of operator error. The remaining variable is the developer solution.

Figure 4. Developing Time Versus Conveyor Speed Setting

Figure 5. Time in System Versus Conveyor Speed Setting

Table 1. Developer Substrate Capacity

Conveyor-Speed Setting	Developing Time (Seconds)	Total Time in System (Seconds)	Capacity,* Substrates/Hour	
			Practical	Theoretical
10	68	172	500	514
20*	36	90	700	1028
30	24	61	700	1440
40	19	46	700	1800
50	15	37	700	2322
60	12	31	700	2880
70	11	26	700	3302
80	9	23	700	3850
90	8	20	700	4285
*Assumes 0.5-inch (12.7 mm) spacing between successive substrates. At speeds greater than 20 it is doubtful that an operator can load the developer fast enough to maintain this substrate spacing.				

Solution Monitoring and Control

The developing solution depletes with continued use. The symptom of the depletion is an increase in the developing time required to achieve complete and consistent development. Consistent development implies the developing action required to achieve satisfactory dimensional control on the HMC pattern. The previously used method of solution control was based on the number of parts processed through the developing solution. The number had been arbitrarily chosen as the number of substrates which could be processed before a 10-percent developing time change. This worked well for immersion developing, but was not considered suitable for spray developing because the developing time normally would not be adjusted (assuming from immersion developing data that the depletion mechanism would be the same).

A different technique was required to determine if the solution was the same from substrate to substrate or from day to day. The test laboratory first suggested a titration technique to measure the alkalinity of the developer (Appendix A). Although the alkalinity test appeared to work well, it required extra apparatus and was not well suited for production use. A quick, simple,

and continuous solution test was needed to provide the operator with a go/no-go resolution. A probe that could be placed in the sump to monitor the solution integrity and provide a continuous go/no-go readout appeared to be the ideal method. Materials Engineering investigated the problem and provided the required test.

Materials Engineering performed an analysis on the developer constituents and on the effect of dissolved photoresist on these constituents (Appendix B). It was found that the color change in the developing solution resulting from the addition of developed photoresist could be correlated to depletion of the ingredients responsible for the developing mechanism. Use of a spectral colorimeter to monitor the solution was recommended. This method was investigated with immersion developing and found to work well. (The spray developer had been purchased, but had not been received at that time.) The light absorbance accurately monitored the developing solution usefulness with immersion processing, and was expected to do the same for spray processing. However, with spray processing there existed a different and unforeseen solution depletion mechanism. This mechanism is unrelated to photoresist interaction with the developer and had not been experienced by any known user of similar equipment.

The developing solution interacts with the air in a way that reduces the ability to develop the resist. Immersion developing containers that were always covered when not in use did not exhibit this trend. Aeration of the solution by the spraying action increases this problem. The solution manufacturer suggested that CO₂ or O₂ was being absorbed in the developer, forming carbonates or peroxides that deactivate the solution. However, Materials Engineering checked for the presence of the carbonates and peroxide and could not distinguish any significant difference between the fresh and depleted solutions. The actual depletion mechanism is still unknown, but has not prevented use of the spray developer for HMC production.

Although the developer life in the 12- to 18-gallon (0.045 to 0.068 m³) machine sump, if air were excluded, might be as long as several months, the life in spray developing is only about two weeks. To reduce the recurring cost of replacing the solution, the sump capacity was decreased to less than 6 gallons (0.022 m³). This did not affect the developing properties of the system. The time the developer solution becomes unusable is determined as shown in Figures 6A through 6C.

Text continues on page 24.

Figure 6A. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Fresh Developer

Figure 6B. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 4 Days

Figure 6C. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 9 Days

Figure 6D. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 14 Days

Figure 6E. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 16 Days

Figure 6F. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 18 Days

Figure 6G. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Developer Age 21 Days

Figure 6 shows the line width deviation* of the photoresist image as a function of the developing time at increasing developing solution age. Increasing the developing action by a longer developing time reduces the total line width of the resist image and produces greater negative deviation. This expected result was confirmed by the positive slope of the line. The family of curves generated by determining the line width change for progressively depleted solutions are quite similar except that each curve representing progressively older solutions is shifted in the positive direction. This shift indicates solution depletion and shows that progressively longer developing times are required to achieve a line width deviation near zero.

It is clear that none of these curves represent linear functions of the machine conveyor-speed setting. The reason is clear in Figure 4, which shows the inverse relationship between conveyor-speed setting and the developing time (also noted along the abscissa of Figure 6). The largest changes in developing time are at the lower end of the conveyor speed setting scale. Therefore, the greatest changes in line width deviation also occur at the lower end of the conveyor speed range. The implications of this nonlinearity and the suggested systematic approach for production use will be discussed later. It is important to conclude from Figure 6 that the developing solution has a usable life with different developing times of about 14-16 days** with near zero line width deviation, and about 21 days with less than 0.2 mil (5.08 μm) deviation. By definition, the acceptable line width deviation is shown by the dashed lines in Figure 6. Solution ages of 14 days or less satisfactorily meet the deviation limits in both the average and sigma boundaries when the developer is used less than one-half hour each day. For that reason the solution should be sprayed for only the minimum time required to develop the photoresist image, and it should be replaced every two weeks. If the solution is aerated by spraying for more than one-half hour each day, the life will be shortened appreciably. Continuous use depletes the solution in less than 12 hours.

*The difference between the mask line width and the developed photoresist image line width. ΔLW = photoresist line width minus the mask line width.

**Based upon less than one-half hour spray usage per day. More than one-half hour spray action will appreciably shorten the usable solution life.

Developer Solution Dilution Ratio

With one exception, the effect of diluting the developing solution with DI water with respect to immersion developing remains essentially the same with spray developing. Diluting the developer decreases the slope and shifts the curves upward (in the positive direction) and to the left (increased developing times). When combined with a fixed maximum developing time, a higher dilution ratio decreases the solution life. For that reason, the necessity of changing the solution more frequently would increase the operating cost.

The results shown in Figure 6 were obtained with a 2:1 developer-to-water ratio and an exposure energy of 0.19 joules/cm^2 . A 2:1 dilution ratio is recommended for production. If the ratio is changed, the usable solution life must be re-established.

Operating Procedures

Since the developing solution depletes too rapidly to operate from day to day at the same conveyor speed, it is necessary to process the substrates at a conveyor speed that compensates for the change in developer strength. The normal point of operation is where the line width deviation versus conveyor speed curve of Figure 6 crosses the zero-deviation line, or just slightly on the positive side, because the resistor can be trimmed to a higher value, but not to a lower value. Experimentation disclosed that the zero deviation point occurs at approximately 80 percent of the chamber length, and is independent of solution strength. This implies that each substrate will receive an over-development equal to the time required to traverse the final 20 percent of the chamber length; however, the line width is not visibly changed during this interval.

It is now possible to establish a production processing technique for developing each substrate in a consistent manner for a near-zero line-width deviation, even though the solution strength may change from day to day. By adjusting the conveyor speed to maintain the development point at 80 percent of the chamber length, each part is properly developed, and any over-development is the same percentage of the basic development time.

For example, Figure 6A shows that a fresh developer solution requires a conveyor speed setting of approximately 60. This corresponds to a development time of 10 seconds. At this setting the conveyor moves at a rate of 2.0 inches per second (50.8 mm/s);

therefore, the time required to complete the last 5 inches (127 mm) of conveyor travel is 2.5 seconds, or 25 percent of the base development time. When the developer has been used for nine days, the curve in Figure 6C shows that the correct zero-deviation conveyor speed setting is approximately 3.0, or a conveyor speed of about 1.0 inch (25.4 mm) per second, and time in the developer is about 19 seconds. Therefore, the time to travel the last 5 inches is 5 seconds, or approximately 25 percent of the total development time. Since the relationship between conveyor speed and speed control setting is linear, this condition is the same at all control settings. Therefore, slowing the conveyor speed is a practical means of providing more time for the partly depleted developer to act on the photoresist, and the development remains the same regardless of reduced developer activity until the development time is extended beyond a practical limit. At that point the minimum conveyor speed is not slow enough to provide the required development time. However, the data in Table 1 show that, even at a speed setting of 1.0, the capacity of the machine is more than adequate for present needs.

The point in the spray chamber at which development is almost complete is maintained by visual observation. Although this is not a precise method and is subject to operator experience, it has provided adequate control.

Because of slight deviations in photoresist thickness and exposure before development, the 25-percent over-development period ensures complete removal over the entire substrate surface, especially on those areas at the extremes of the deviation distributions. This is shown graphically by the ± 1 -sigma limits in Figure 6. Even though the operator might miss the 80-percent development point by as much as 10 percent, the total line-width deviation does not change more than 50 microinches (12.7 μm). This is less than one-half of the standard deviation expected from normal processing.

Spray Pressure

Within the usable range of spray head pressures the average quantitative deviation in line width is not significantly altered, but the spray pressure does affect the uniformity of the spray distribution in the chamber; therefore, it influences the line width deviation distribution across the substrate. If the spray is not uniform, there will not be an even developing action across the chamber as the substrates move through on different paths. This widens the process line-width variation. For that reason the spray pressure controls should be fully open.

Solution Temperature

The solution temperature is normally maintained between 68 and 77°F (20 to 25°C). Although an elevated solution temperature increases the developing action and reduces the development time, it also causes the solution to evaporate more rapidly and thereby alters the solution concentration, which in turn, influences the dimensional quality of the pattern. Therefore, rather than being heated, the developing solution should be maintained at room temperature (20 to 25°C).

Although not heated, the solution temperature will rise because of heat generated by the pump. If the pump is operated for more than two hours continuously, a temperature rise of 2 to 5°C can be expected. There are no provisions in the system to cool the solution; therefore, if the solution increases above 80°F (26.7°C), the conveyor speed setting should be adjusted to allow for the increased developing action. If it becomes necessary to operate the system continuously, cooling coils should be added to the developer sump.

It is recommended that production parts be so arranged that all first level patterns, second level patterns, and reworked HMCs are processed through the developer in large groups.

Photoresist Exposure and Developing Relationship

The resist exposure and developing processes are interrelated as shown in Figure 7. With increasing exposure energy, less developing time is required to hold the same line-width deviation; a longer developing time is required for reduced exposure energy. Within certain latitudes, one process appears to compensate for process errors in the other. This is true for a manually controlled operation; however, for large-volume, automated processing it is not practical to consider process-error compensation. The optimum operating point must be determined by evaluating the combined process error and error distribution for all process steps: resist thickness, prebake time/temperature, exposure energy, developing time, and etching times. When this is done, a statement of total line-width-deviation distribution can be made. The data in Figures 6 and 7 do not reflect the effects of previous process variations, but were adjusted to show only the influence of the developing process on the line-width deviation. Without such adjustment, these curves would appear as shown in Figure 8, which show what can be expected in photoresist line-width deviation as a result of process variations in roller coating, drying, exposure, and developing.

Text continues on page 34.

Figure 7A. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Exposure Six Seconds

Figure 7B. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Exposure Eight Seconds

Figure 7C. Photoresist Line-Width Deviation Versus Conveyor Speed Setting, Exposure Ten Seconds

Figure 8A. Line-Width Data Not Compensated for Photoresist Thickness Variation, Exposure 6 Seconds

Figure 8B. Line-Width Data Not Compensated for Photoresist Thickness Variation, Exposure 8 Seconds

Figure 8C. Line-Width Data Not Compensated for Photoresist Thickness Variation, Exposure 10 Seconds

Total Process Deviations

Figures 9 through 13 show the total expected photoresist line-width deviation resulting from variation in developing, exposure, prebake temperature, and resist thickness. (Resist thickness variation is the major contributor to the large line-width distribution.)

Because the conveyor speed does not change more than one percent after the controller is set, the line-width change caused by speed variation is less than 20 microinches ($0.5 \mu\text{m}$). Since the exposure energy also is constant to ± 4 percent, the expected line deviation is less than ± 0.025 mils ($\pm 0.635 \mu\text{m}$). However, the resist thickness variation of $\pm 0.6 \mu\text{m}$ at a constant machine setting can result in a ± 0.12 -mil ($\pm 3 \mu\text{m}$) deviation in the line width.

Figure 9. Photoresist Thickness and Line-Width Variations, Conveyor Speed 10

Text continues on page 37.

Figure 10. Photoresist Thickness and Line-Width Variations, Conveyor Speed 20

Figure 11. Photoresist Thickness and Line-Width Variations, Conveyor Speed 40

Figure 12. Photoresist Thickness and Line-Width Variations, Conveyor Speed 60

Figure 13. Photoresist Thickness and Line-Width Variations, Conveyor Speed 80

The Figures 9 through 13 show the expected line-width deviation at various locations on the substrate at different developer speeds. The change in line width across the substrate shows that across any one 3.75- by 4.5-inch (95 by 114 mm) substrate, a 5-mil (127 μ m) wide resistor may vary as much as ± 3 percent of the designed width. This information is also represented by the ± 1 -sigma limits shown in Figures 7 and 8. Typical variations in resistor line widths can be expected to be in the ± 4 percent range, where ± 2 to 3 percent of this value is the result of process variations in photoresist processing. The major contributor, resist thickness variation, is the area where additional effort should be made.

Facilities Considerations

The spray development experience gained in this work indicates that the following features should be incorporated when installing the spray development machine for production use.

- Venting should be provided for the system at 200 cfm (94.4 dm³/s) at each port. It should be vented only while the system is spraying.
- The floor areas should be protected from spills for at least 12 inches (0.3 m) around the entire system. The floor area also should have provision for containing the spill. A drain in the contained spill area should be provided.
- Since the developer is mildly basic, pH $\approx$ 12, adequate drains should be provided to empty the sump. The fluid should not be drained into chemical waste containers as this would not be an economical procedure.
- The spray chamber and sump area should be continuously purged with N₂ to a slight positive pressure to prevent oxygen from contacting the developing fluid. This is particularly important during spraying.
- The deionized water required for rinsing should be more than 5 megohms/cm and relatively particulate free. The water temperature should be maintained very near room temperature, particularly if Riston is used to "tent" vias (plated-through-holes) in the substrates.

ACCOMPLISHMENTS

All of the objectives outlined in the original development plan have been attained:

- The system characteristics have been defined for transfer to production;
- A developing schedule has been established; and
- The process information has been transferred to Process Engineering.

FUTURE WORK

Additional technical development work is not required on the existing photoresist and developer (AZ1350J and AZ, respectively) for use with the DEA spray system and the recommended operating procedure; however, an effort should be made to reduce operating cost. Changing the developer solution every two weeks will cost approximately \$80 per month. There are three measures that can be expected to reduce costs:

- Formulate a developing solution that does not degrade in air;
- Design a solution monitor and positive feedback mechanism to control the conveyor speed as a function of the developer strength; and
- Design a spray developing system with sufficient solution capacity for a single shift operation, or a system that uses the solution only once.

A specially-designed spray system appears to offer the most feasible approach, with the lowest investment in time and materials.

If the photoresist used in production is changed, additional development effort will be necessary. A backup photoresist capability has been suggested.

The DEA spray developing system is not the optimum approach to production spray processing of hybrid microcircuits; therefore design and development of special spray processing equipment is recommended to make more efficient use of floor space, operator time, and solution capacity.

Appendix A

A PROCEDURE FOR TESTING AZ
PHOTORESIST DEVELOPER TO
DETERMINE THE STATE OF
DEPLETION

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A PROCEDURE FOR TESTING AZ PHOTORESIST DEVELOPER TO DETERMINE THE STATE OF DEPLETION

A quantitative analysis by the Materials Test Laboratory shows that AZ photoresist developer is a mixture of sodium hydroxide, trisodium phosphate, and sodium metasilicate. The sodium hydroxide is the active ingredient; the other two act as buffers to control the alkalinity of the solution. Because of the buffering action of the phosphate and metasilicate, the pH does not change significantly during the useful life. Analysis of fresh and used (depleted) samples showed that the solution is approximately 36-percent less alkaline when approaching depletion.

To provide a means of monitoring the developing solution during production, the following test procedure was developed:

- Place a 10-ml aliquot of sample into a 250-ml beaker.
- Dilute the sample to 100 ml with deionized water.
- Add 8 drops of phenolphthalein indicator solution (1-percent solution of phenolphthalein in ethyl alcohol).
- Titrate the red solution with a 0.1-normal hydrochloric acid solution until the solution no longer appears pink.
- Calculate the alkalinity as follows:
$$\text{milliequivalents of alkalinity} / 10 \text{ ml} = \text{ml acid} \times \text{acid normality}.$$
- Compare the alkalinity of a fresh solution and a used solution to determine the relative usability of the used solution.

Since this method requires little time and only a small sample of the solution, it is well suited for use in production.

Appendix B

A METHOD OF MONITORING DEVELOPER
CONDITION DURING USE

Appendix B

A METHOD OF MONITORING DEVELOPER CONDITION DURING USE

A parameter of the solution which could be correlated to the deterioration of developing quality with use was sought. To select some parameter that could be readily monitored the composition of the developer solution had to be determined.

The components of AZ photoresist developer are sodium ions, Na^+ ; orthophosphate ions, PO_4^{3-} and HPO_4^{2-} ; and metasilicate ions, SiO_3^{2-} . The solution probably was prepared by dissolving Na_3PO_4 , Na_2HPO_4 , and Na_2SiO_3 in water. The final concentrations are 0.7 molar Na^+ , 0.14 molar PO_4^{3-} plus HPO_4^{2-} , and 0.21 molar SiO_3^{2-} . The orthophosphate and metasilicate ions act as buffers to keep the pH from changing rapidly.

The presence of the two buffering agents was determined by titrimetry. The orthophosphate was identified by precipitation as ammonium molybdophosphate, a bright yellow precipitate, and was determined quantitatively by a standard procedure involving the same precipitation process. The sodium ions and the silicon in the metasilicate ions were detected and analyzed by atomic absorption spectrophotometry (AA). The silicon-containing component was determined to be metasilicate by correlating the titrimetry experiments with existing information on known silicate compounds.

Potassium ions were eliminated by AA and ammonium ions were eliminated by a standard test. All other cations were eliminated by the fact that they form insoluble compounds with orthophosphate. Borate ions were eliminated as a buffering agent with an AA test for boron. Since sodium was the only cation present and the sodium concentration corresponded to the orthophosphate and metasilicate concentrations, significant amounts of other inorganic anions were absent. Attempts to separate any organic components by acidification, solvent extraction, and crystallization gave negative results.

Experience has indicated that the pH of the solution does not change significantly during use, and would not be satisfactory for monitoring the solution. A determination of the decreasing buffer capacity of the solution by titration would not be satisfactory due to possible interferences from products of the developing process and the solution color. The solution color was considered a good parameter to monitor because it becomes darker with use.

The first problem was to determine if the solution color changed significantly during its useful life. A Beckmann DU Spectrophotometer

was used to measure the absorbance of two used developer solutions. Absorbance is defined as $\log I_0/I_t$, where I_0 is the intensity of an incident light beam and I_t is the intensity of the transmitted light. The results are shown in Figure B-1. Sample B had been used only a short time, and was light brown in color. Sample C was obtained by diluting Sample B 1:3 with developer solution. Sample A was taken from a solution discarded the following day because of deterioration. The change in absorbance between the solutions is sufficient for use in monitoring used developer solutions.

Figure B-1. Developer Solution Absorbance Versus Light Wavelength

Figure B-1 also shows the change in absorbance with wavelength for the three concentrations. This relationship is used to determine the best wavelength for measuring concentration changes. Normally, the wavelength at a maximum is used. However, in this case, the maximum for Sample A was off scale. Absorbance scales of commercial instruments stop at 2.0. If Sample A is at least temporarily used as a standard for discarding solutions, a wavelength for which curve A is on scale must be used.

A wavelength of 400 nm was used to monitor the accumulation of resist in the developer solution. Ten 2-inch (50.8 mm) square alumina substrates coated with 3 to 3.5 μm thick AZ-1350 photoresist were placed one at a time in 100 ml of developer until all of the photoresist was dissolved. The solution was stirred slightly. The substrates were weighed before and after as the resist was removed. The absorbance of the developer solution was measured after each substrate had been stripped of resist. The time required for resist removal was measured with a stopwatch. The results are given in Table B-1.

Table B-1. Absorbance Data

Panel	Weight of Resist Removed (g)	Total Resist in Solution (g/l)	Removal Time (minutes)	Absorbance
1	0.0062	0.062	0.58	0.177
2	0.0064	0.126	0.56	0.368
3	0.0065	0.191	0.66	0.552
4	0.0064	0.255	0.56	0.750
5	0.0064	0.319	0.56	0.973
6	0.0063	0.382	0.56	1.20
7	0.0065	0.447	0.59	1.43
8	0.0065	0.512	0.75	1.66
9	0.0069	0.581	0.56	1.95
10	0.0068	0.659	0.52	2.00+

The resist concentration in the developer is plotted against absorbance in Figure B-2. These data demonstrate the use of absorbance to monitor developer solution usage, and show some correlation of absorbance to the quantity of resist dissolved in the developer. The correlation is not precisely quantitative

Figure B-2. Absorbance Versus Photoresist Concentration in the Developer Solution

because the solution color is affected by light and the resist concentrations may be slightly low. The developer volume used to calculate resist concentrations was assumed to remain constant, but in reality, it was decreasing slightly due to dragout when removing panels and solution loss when samples were removed for measuring the absorbance and then returned.

The developing times given are approximate measurements because the developing process was monitored visually and development was determined by triggering a stopwatch when all of the resist on a panel appeared to be dissolved. The developing times varied, but the time for the tenth panel was about the same as for the first. However, the developing properties on a microscale may

be different from that on a macroscale. The problem may be one of changing surface tension or viscosity, and may be magnified when developing microcircuit patterns. These solution properties are functions of resist concentration in solution that can be measured spectrophotometrically.

Spectrophotometric measurement of solution absorbance is recommended to monitor the developer solution during use. A wavelength of 400 to 450 nm should be used. The absorbance value at which the solution must be discarded is somewhere near curve A in Figure B-1. The exact value must be determined by processing experience.

Two types of commercially available spectrophotometers may be considered. The Bausch & Lomb equipment is the most common type, and can be used with a flow-through sample cell for continuous monitoring. The Brinkmann instrument is a new type which also permits continuous monitoring. Either instrument must be calibrated periodically to read zero absorbance for the unused developer solution.

Appendix C

PHOTOLITHOGRAPHY TECHNOLOGY
TRANSFER PLAN

Appendix C

PHOTOLITHOGRAPHY TECHNOLOGY TRANSFER PLAN

The philosophy of this spray processing is one of *imaging*, rather than the more-conventional *dimension-control concept*. The principal differences in these two techniques are in the degree to which geometric dimensions are controlled and in the method of control. With the dimension-control method, the photolithography parameters are rigidly controlled to maintain a maximum ± 1 -percent line-width variation on 5.0-mil (0.127 mm) lines. Because of large variations in the sheet resistivity of Ta₂N films and the limited production capability of the resistor trimming facilities, this approach is placing excessive demands on present photolithography facilities, particularly on the photoresist and etching processes. For that reason, improved photoresist and etching techniques are necessary.

The imaging concept relaxes the control limits to (± 1 sigma) of the design line width. However, the imaging method is more a matter of definition than of actual change in dimension control. The machine settings remain essentially unchanged, but line width is allowed to vary as much as 5 percent more than the nominal width. The normal ± 1 sigma variation corresponds closely to ± 1 percent deviation on 5-mil lines because the process is not changed significantly--only the criteria for evaluating the result is changed. Therefore, the ± 1 sigma deviation can be expected to represent ± 1 -percent of line width, or ± 0.0001 inch (2.54 μm). This change in philosophy does not alter the photolithography specification, but permits processing to take advantage of the natural lenient properties of the photoresist.

The planned transfer of the spray processing equipment to production is outlined in Figure C-1, Engineering and process development before the transition will include the following:

- Engineering personnel responsible for the process development will provide base-line data and prepare specifications before the transition start dates, and all known facilities considerations will be passed on to Process Engineering.
- Information exchanges with Product Engineering and Sandia Laboratories during the interval before the transfer dates will provide time for necessary specification changes and approval for use before commitments are made.
- Process Engineering will characterize the equipment before the transfer date and will prepare operating procedures and processing instructions.

The machines and equipment to be transferred to production on the time schedule shown in Figure C-1 consist of the following items:

1. Roller Photoresist Coater,
2. Infrared Oven,
3. Cobilt Autoaligner,
4. Spray Photoresist Developer,
5. Chromium/Gold Spray Etcher,
6. Tantalum-Nitride Spray Stripper, and
7. Tantalum-Nitride Spray Etcher.

The roller photoresist coater and the infrared oven (Items 1 and 2) are already in the production area.

There is some question at this point on use of the Cobilt Auto-aligner (Item 3) automatic alignment feature. A decision based on comparison of increased processing capability and the cost of masking target areas before Ta₂N sputtering will be made by Process Engineering by December 1, 1973. (The automatic alignment feature will not handle Cr/Au/Ta₂N-substrates as they are described in present purchasing specifications). If the auto alignment feature is used, L. E. Schantz will provide the necessary base-line data. The machine will be returned early in January 1974 to the Cobilt Corporation for modification as directed by L. E. Schantz.

The spray photoresist developer (Item 4) transfer plan requires the following work:

- A solution monitoring method must be devised to provide a continuous indication of the developer condition--the number of days the solution will remain usable or the number of substrates that can be processed before solution replacement is necessary. This monitoring method and the equipment required will be determined before the transfer.
- A workable range of developer concentrations, developer-to-water ratio, will be determined.
- A suitable range of development time or machine settings and the optimum spray pressure for each conveyor speed will be determined.

The Cr/Au/etcher, the Ta₂N stripper, and the Ta₂N etcher (Items 5, 6, and 7) require suitable methods of continuously monitoring the solutions to indicate the number of days the solutions will remain

Figure C-1. Photolithography Equipment and Technology Transfer Schedule

usable or the number of substrates that can be processed before replacement is necessary. A processing envelope within which acceptable yields can be obtained will be necessary for each machine to establish usable ranges of machine control settings. these processing envelopes will provide the balance of conveyor speed and spray pressure that is necessary to maintain line-width deviation within specified limits.

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