

## Positive Dye Photoresist Compositions With 2, 4, 6-tris (phenylazo) resorcinol and phenyl-1, 3-bis (azo resorcinol) Dyes

Dipak Kumar Mukhopadhyay

Institute of Science & Technology, C.K.Town, West Bengal, 721201, India

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**Abstract:** Novolac resin with the mixture of ortho, meta and para cresol has been synthesized. 1-oxo-2 diazo naphthalene-5-sulfonyl chloride has been synthesized and its corresponding sulfonate esters with 2,3,4-trihydroxy benzophenone, 2,4,6-trihydroxy benzophenone, 4,4'-dihydroxy diphenyl sulfone and the corresponding sulphonamides with 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl sulfone have been synthesized. Two new azo dyes namely 2,4,6-tris (phenylazo) resorcinol and phenyl-1,3-bis (azoresorcinol) have been synthesized. The photoresist film have been casted on silicon wafer by mixing novolac resin, diazonaphthaquinone sulfonate esters or sulphonamides and the corresponding azo dye in the solvent mixture of acetone, xylene and ethyl acetate. After soft baking, the film are irradiated upon UV radiation exposure. After irradiation, the exposed regions are soluble in aqueous alkaline developer.

**Key Words:** Novolac resin, 1-oxo-2-diazo naphthalene-5-sulfonyl chloride, sulfonate esters, sulphonamides, 2,4,6-tris (phenylazo) resorcinol dye, phenyl-1,3-bis(azo resorcinol) dye, UV irradiation.

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### I. Introduction:

Microcircuit fabrication requires that precisely controlled quantities of impurities be introduced into tiny regions of the silicon substrates, and subsequently these regions must be interconnected to create components and VLSI circuits. The patterns that define such regions are created by lithographic processes in which layers of photoresist materials are spin-coated onto the wafer substrates. The resist layer is selectively exposed to a form of radiation, such as ultraviolet light, electrons, or x-ray using an exposure tool and mask to effect the desired selective exposure. The patterns in the resist are formed when the resist is developed so that the areas of resist remaining after development protect the substrate regions which they cover. Locations from which resist has been removed are subjected to one or more additive or subtractive processes that transfer the pattern onto the substrate surface.

The photoresist is applied as a thin film to the substrate, and subsequently exposed through a mask. The mask contains clear and opaque features that define the pattern to be created in the PR layer in which areas exposed to the light are made either soluble or insoluble in a specific solvent known as a developer. In the case when the exposed regions are soluble, a positive image of the mask is produced in the resist (positive resist). If the non irradiated regions are dissolved, a negative image results (negative resist). The resist performs two roles in this process. First, it must respond to exposing radiation in such a way that the mask image can be replicated in the resist. Second, the remaining areas of resist must protect the underlying substrate during subsequent processing. Although both negative and positive optical resist are used to manufacture semiconductor components, the higher resolution capabilities of positive resist have virtually made them the exclusive choice for VLSI applications. Conventional positive optical lithographic processes and resist are capable of producing images on VLSI substrates with submicron dimensions. For smaller features, however, diffraction effects during exposure may ultimately cause other higher-resolution techniques to replace optical lithography.

Conventional optical photoresist are three-component materials consisting of: (1) the matrix material (also called resin), which serves as a binder, and establishes the mechanical properties of the film. (2) The sensitizer (also called the inhibitor), which is a photoactive component (PAC). (3) The solvent (different than the developer solvent), which keeps the resist in the liquid state until it is applied to the substrate being processed. The matrix material is usually inert to the incident imaging radiation such that it does not undergo chemical change upon irradiation, but provides the resist film with its adhesion and etch resistance, it also determines other film properties of the resist such as thickness, flexibility, and thermal flow stability. The sensitizer is the component of the resist material that reacts in response to the actinic radiation.

The resolution of a lithographic process is formally defined in terms of the modulation transfer function of the lithography exposure equipment and how well it is matched to the resist being utilized. The resolution of a lithographic process can be limited by many aspects of the process, including: hardware, optical properties of the resist material, process characteristics.

Positive photoresist for microelectronics applications are three-component materials (i.e. matrix, sensitizer, and solvent), whose properties are altered by the photochemical transformation of the photosensitive component, from that of a dissolution inhibitor to that of a dissolution enhancer. The matrix component of

positive resists is a low –molecular weight novolac resin which forms the resist film properties .The novolac resin dissolves or disperses in an aqueous base such as the developer. The sensitizers or photoactive compounds (PAC) in positive photoresists are photosensitive , but are insoluble in aqueous developer solution and also therefore prevent the novolac resin from being dissolved by the developer. Upon exposure to light ,the sensitizers which prior to exposure act as dissolution inhibitors, photochemically decompose and allow the novolac resin to dissolve. Unexposed regions remain much less soluble in developer which is the primary mechanism for image formation in positive resist. Positive photoresists have become the dominant resists for VLSI applications because of their higher resolutions which arise because the unexposed film regions are not permeated by the developer.

In this invention a base soluble novolac has been used as a matrix material and diazonaphthaquinone sulfonate esters of 2,3,4-trihydroxy benzophenone,2,4,6-trihydroxy benzophenone and 4,4'-dihydroxy diphenyl sulfone and diazonaphthaquinone sulphonamides of 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl sulfone have been used as photoactive compounds. As photo extinction agent two new azo dyes namely 2, 4, 6-tris (phenylazo) resorcinol and phenyl-1, 3-bis (azo resorcinol) have been used. The positive photoresist compositions and processes provided in this invention dramatically improved performance properties on reflective semiconducting substrates while maintaining adequate photospeed. Photoresist absorbance in this compositions is increased by the addition of two dyes mainly 2,4,6-tris(phenylazo) resorcinol and phenyl-1,3-bis (azoresorcinol).These two dyes enhanced the dissolution rate of the exposed photoresist in developer because the dyes contain more phenolic hydroxyl groups.

## **II. Experimental:**

### **2.1. Preparation of Novolac resin from the mixture of ortho,meta and para cresol:**

A one liter four-neck resin kettle equipped with a stirrer,heating source,thermometer, variable reflux ratio distilling head and a nitrogen inlet tube was charged with 70.0g meta cresol,84.0g para cresol, 9.0g ortho cresol, 17.0g of 36.9% formalin,5ml deionized water and 3.0g oxalic acid dihydrate.The mixture was heated to about 60<sup>0</sup>c at which point an exothermic condensation reaction ensured. When the reaction mixture temperature reached about 100<sup>0</sup>c ,68.0g of 36.9% formalin was added in about 30 minutes .The reaction was then allowed to continue for about 4 hours at reflux temperature. The more volatile components in the reaction mixture were removed by distillation at ambient pressure under a constant flow of nitrogen. When the temperature of the reaction mixture reached about 220<sup>0</sup>c ,a partial vacuum pressure was applied and was gradually increased until a maximum vacuum of 7mm Hg was achieved, and the mixture was at about 228<sup>0</sup>c .The liquefied resin remaining in the kettle was poured into a tray under nitrogen and allowed to cool and solidify.

### **2.2 Preparation of 1-oxo-2 diazo naphthalene-5-sulfonyl chloride:**

3.0g of sodium 1-diazo -1,2-naphthaquinone -5-sulfonate was taken in a foil covered flask.14ml of chlorosulfonic acid was carefully added to the flask so as to maintain the reaction temperature below 60<sup>0</sup>c. The reaction mixture was heated with stirring for 30 minutes at 65<sup>0</sup>-70<sup>0</sup>c .the mixture was then allowed to cool in an icebath and added 100ml of cold water dropwise such that the reaction temperature did not exceed 75<sup>0</sup>c .The yellow precipitate of 1-diazo -1,2-naphthaquinone-5 –sulfonyl chloride was collected with vacuum filtration.

### **2.3 Preparation of sulfonate esters and sulphonamides of 1-oxo-2-diazo naphthalene-5-sulfonyl chloride:**

#### **2.3.1. Preparation of ortho naphthaquinone diazide sulfonate ester of 2,3,4-trihydroxy benzophenone:**

To a 250ml flask equipped with a constant temperature bath, thermometer, magnetic stirrer were added 11.0g (0.05mols) of 2, 3,4-trihydroxy benzophenone, 15.9g (0.05mols)of 1-oxo-2-diazo naphthalene-5-sulfonyl chloride and 200ml reagent grade acetone. While the mixture was maintained at 30<sup>0</sup>c ;28.5g of 12% sodium carbonate was added drop wise over 10 minutes ,after the base addition, the reaction mixture was allowed to stir for 30 minutes at about 30<sup>0</sup>c .5ml of concentrated hydrochloric acid was then slowly added to the mixture while keeping its temperature at 30<sup>0</sup>c. The reaction solution was filtered to remove the bulk of sodium chloride and the filtrate was added to 1000ml 1% hydrochloric acid. The precipitated solid was stirred for 1 hour, filtered and collected.

#### **2.3.2. Preparation of ortho naphthaquinone diazide sulfonate ester of 2,4,6-trihydroxy benzophenone:**

To a 250ml flask equipped with a constant temperature bath, thermometer ,magnetic stirrer were added 11.5g (0.05mols) of 2,4,6-trihydroxy benzophenone, 13.4g (0.05mols) of 1-oxo-2-diazo naphthalene -5-sulfonyl chloride and 200ml of reagent grade acetone. while the mixture was maintained at 30<sup>0</sup>c, 28.0g of 12% sodium carbonate was added dropwise over 10 minutes .After the base addition the reaction mixture was allowed to stir for 30minutes at 30<sup>0</sup>c .5ml concentrated hydrochloric acid was then slowly added to the mixture while keeping its temperature at 30<sup>0</sup>c.The reaction solution was filtered to remove bulk of sodium chloride and the filtrate was added to 1000 ml 1% hydrochloric acid. The precipitated solid was stirred for 1 hour, filtered and collected.

### 2.3.3 Preparation of ortho naphthaquinone diazide sulfonate ester of 4,4'-dihydroxy diphenyl sulfone:

To a 250 ml flask equipped with a constant temperature bath, thermometer, magnetic stirrer were added 12.5g (0.05mols) of 4,4'-dihydroxy diphenyl sulfone, 13.4 g (0.05mols) of 1-oxo-2-diazo naphthalene-5-sulfonyl chloride and 200ml reagent grade dioxane. while the mixture was maintained at 30<sup>0</sup>c, 28.5g of 12% sodium carbonate was added drop wise over 10 minutes. After the base addition, the reaction mixture was stirred for 30 minutes at 30<sup>0</sup>c. 5 ml concentrated hydrochloric acid was then slowly added to the mixture while keeping its temperature at 30<sup>0</sup>c. The reaction solution was filtered to remove bulk of sodium chloride and the filtrate was added to 1000ml 1% hydrochloric acid. The precipitated solid was stirred for 1 hour, filtered and collected.

### 2.3.4. Preparation of ortho naphthaquinone diazide sulphonamide of 4,4'-diamino diphenyl methane:

In a 250 ml flask equipped with constant temperature bath, thermometer, magnetic stirrer were added 13.4g (0.05mols) diazonaphthaquinone sulfonyl chloride, 9.9g (0.05mols) of 4,4'-diamino diphenyl methane and 200ml reagent grade tetrahydrofuran. The reaction mixture was stirred for 30 minutes at 30<sup>0</sup>c. To this reaction mixture 6 ml triethylamine was added dropwise with stirring and allowed to stir for 1 hour. The reaction mixture was then poured into 500 ml of cold water and chilled in ice bath to precipitate out the product. The product was collected using vacuum filtration, air dried and washed with petroleum ether.

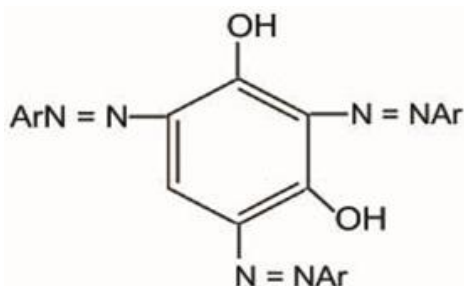
### 2.3.5 Preparation of ortho naphthaquinone diazide sulphonamide of 4,4'-diamino diphenyl sulfone:

In a 250 ml flask equipped with constant temperature bath, Thermometer, magnetic stirrer were added 13.4g (0.05mols) of diazonaphthaquinone sulfonyl chloride, 12.4g (0.05mols) of 4,4'-diamino diphenyl sulfone and 200 ml reagent grade dioxane. The mixture was stirred for 30 minutes at 30<sup>0</sup>c. To this reaction mixture 6 ml triethyl amine was added drop wise with stirring and allowed to stir for 1 hour. The reaction mixture was then poured into 500ml of cold water and chilled in a ice precipitate out product. The product was collected using vacuum filtration, air dried and washed with petroleum ether.

## 2.4. Preparation of azo dye:

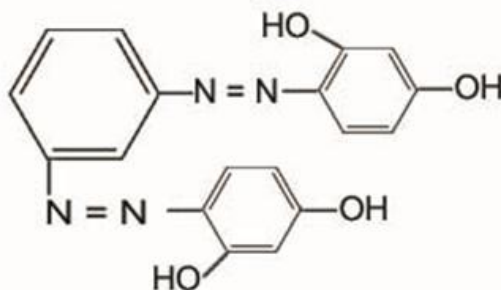
### 2.4.1. Preparation of 2, 4, 6-tris (phenyl azo) resorcinol:

In a 500 ml beaker, 7.5g of aniline was added to 40 ml of water, and to this solution was added 20 ml of concentrated hydrochloric acid and the solution was cooled to 5<sup>0</sup>c. 9.4g of isoamyl nitrite was then added slowly. In a second 500 ml beaker, 10.0 g of sodium acetate was added to a stirred solution of 2.2 g of resorcinol in 40 ml water and dissolved. Then the above diazonium solution was added in a thin stream to the resorcinol solution with vigorous stirring. stirring continued for 2 h, and dyes precipitated out. After that the dye was filtered off and washed with water and collected.



### 2.4.2. Preparation of phenyl-1, 3-bis (azo resorcinol):

In a 500 ml beaker, 5.4 g of 1,3-diamino benzene was dissolved in 30 ml of concentrated hydrochloric acid and then 40ml of water was added and solution was cooled to 5<sup>0</sup>c. 15.0 g of isoamyl nitrite was then added slowly. In a second 500ml beaker 40.0 g of sodium acetate was added to a stirred solution of 11.0 g of resorcinol in 130 ml of water and dissolved. Then the above diazonium solution was added in a thin stream to the resorcinol solution with vigorous stirring. Stirring continued for 1 hour and then the dye was precipitated out. After that the dye was filtered off washed with water, dried and collected.



## 2.5. Photoresist Compositions with different dye compounds:

### Example-1

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulfonate ester, 0.2g of 2, 4,6-tris(phenylazo) resorcinol dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7 g of ethylacetate, The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100<sup>0</sup>c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

### Example-2

A photoresist composition was prepared by dissolving 2.4g of naphthaquinone diazide sulfonate ester, 0.2 g of phenyl-1, 3-bis(azoresorcinol) dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7 g of ethyl acetate. The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100<sup>0</sup>c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

### Example-3

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulphonamide, 0.2 g of 2,4,6-tris (phenylazo) resorcinol dye and 9.9 of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7 g of ethyl acetate. The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100<sup>0</sup>c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in near ultra violet region, in any desired exposure pattern by using suitable masks, stencils, templates etc. The exposed ,resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

### Example-4.

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulphonamide, 0.2 g of the phenyl-1, 3-bis (azo resorcinol) and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7g of ethyl acetate. The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100<sup>0</sup>c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc .The exposed resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

## III. Result and Discussion:

The following combination of properties of the novel dyed positive photoresist compositions of the present invention are distinctly better than the photoresist compositions of the prior art : (1) The novel dyes namely 2,4,6-tris (phenyl azo) resorcinol and phenyl-1,3-bis (azoresorcinol) are soluble in aqueous alkaline developer and does not significantly inhibit the dissolution rate of the exposed photoresist film in aqueous alkaline developer. (2) The dyes do not significantly harm deep-UV curing processes of the photoresist film. (3) The dyed photoresist composition have substantially better resolution . (4) The dyed photoresist compositions require less exposure energy than prior dyed photoresist compositions. (5) The novel dyes are non-volatile and are not readily sublimed from the resist film and (6) The novel dyed photoresist compositions are stable for at least one year without forming precipitates.

The new positive photoresist compositions containing aqueous alkaline soluble 2,4,6-tris (phenylazo) resorcinol and phenyl-1,3-bis (azo resorcinol) dyes which have the advantage of high resolution, improved photo speed, deep-UV curable and high absorbance, excellent stability, non-volatility and patterning method using the compositions of the present invention.

The present invention provides novel photoresist compositions which contain highly absorbant actinic 2,4,6-tris (phenylazo) resorcinol and phenyl-1,3-bis (azo resorcinol) dyes highly soluble in both casting solvent and aqueous alkaline developer, high resolution novolac resin, and high resolution photoactive component with several diazoquinone groups per molecule dissolved into safer solvents with high solvency power. The compositions of the present invention have the advantages of high resolution capability, improved control of refraction effects, high unexposed film thickness remaining after development increased photoresist stability and low require exposure does. Enhancing the actinic absorbance of positive photoresist diminishes undesirable reflection phenomenon. The absorbance at wavelength of irradiation can be enhanced through the addition of dye to the photoresist. The optimal dye should have the following properties: highly absorbing from 365 nm to 436 nm in the spectral region to allow use of the same composition on a variety of photolithographic exposure equipment, high solubility in the photoresist solvent, self-life of at least 6 months, solubility in aqueous alkaline developer, does not sublime significantly during baking process, does not significantly harm deep-UV curing processing and does not reduce significantly the dissolution rate of exposed photoresist in developer solution.

The 2,4,6-tris (phenylazo) resorcinol and phenyl-1,3-bis (azoresorcinol) dyes used in the compositions of the present invention have good solubility in the casting solvent and aqueous alkaline developer. Solubility in the casting solvent is a complex chemical phenomenon that depends upon the chemical nature of the individual photoresist components, including the chemical functionality, type and nature of bonding, polarity, flexibility and shapes of the solvent and dye molecules. Solubility in the aqueous alkaline developer is primarily determined by the type and the number of the acidic hydrophilic groups. Examples of acidic hydrophilic substituents include acid groups and hydroxyl groups. The location and intensity of the ultraviolet/visible absorption spectrum of the dye is determined by the electronic nature of the individual dye molecule and its interaction with the other molecules in the photoresist compositions.

The most preferred solvent composition of this invention are blends of acetone, xylene and ethyl acetate. These solvents give a useful combination of low required exposure does, good solvency low toxicity and useful volatility.

The most preferred compositions of the present invention include from about 75 to about 92 percent of a mixture of base soluble phenolic resin and a dye or mixture of dyes, the proportion by weight of said dyes are about 0.4 percent to about 8 percent of the weight of resin and from about 8 to about 25 percent of a naphtha quinone diazide sulfonate ester or sulphonamide.

#### **IV. Conclusion:**

This article summarizes the recent development of positive dye photoresist composition with two novel azo dyes namely 2,4,6-tris (phenylazo) resorcinol and phenyl-1,3-bis (azoresorcinol). This novel positive dyed photoresist are distinctly better than the photoresist composition of the prior art. The novel two dyes are soluble in both the casting solvent and also in aqueous alkaline developer. The dyes do not significantly harm deep UV-curing process of photoresist film. The novel dyed photoresist compositions have substantially better resolution and require less exposure energy. The novel dyes are non-volatile and are not readily sublimed from the resist film. The mixture of casting solvent is new and cheaper. These solvent have little toxicity, good solvency and useful volatility. The new aqueous alkaline developer used here is 0.25 (M) tetramethyl ammonium hydroxide which does not form scum on the exposed semiconductor substrates.

#### **References:**

- [1]. C.A.Mack "Analytical Expression for the standing wave intensity in photoresist", Appl.opt.,vol.25,No.12,1986,pp. 1958-1961.
- [2]. S. Middlehoek, "Projection Masking, Thin photoresist Layers and interference Effects," IBM Jour.Res.Dev.,vol.14,1970,pp.117-124.
- [3]. J.E.Korka, "standing waves in photoresist", Appl.opt.,vol.9,No.4,1970,pp.969-970.
- [4]. D.F.Ilten and K.V.patel, "standing wave effects in photoresist Exposure," Image Technology (Feb/Mar.,1971) pp.9-14.
- [5]. E.J. Walker, "Reduction of the standing-wave Effect by post-Exposure Bake," Trans.Electron Dev.,vol.ED-22,No.7.1975,pp.464-466.
- [6]. T.Batchelder and J.Piatt, "Bake Effects in positive photoresist," solid state Tech.,vol.26, NO.8,1983,PP.211-217.
- [7]. T.Brewer,R.Carlson and J.Arnold, "The Reduction of the Standing-wave Effect in positive photoresist," Jour.Appl.photogr.Eng.,vol.7,No.6,1981,pp.184-186.
- [8]. Y.C. Lin,etal., "some Aspects of Anti-Reflective coating for optical Lithography," Advances Resist Tech.,proc.,SPIE,Vol.469,1984,pp.30-37.
- [9]. C.A.Mack, "Modeling the Effects of prebake on positive Resist processing," Kodak Microelec. seminar interface,1985,pp.155-158.
- [10]. A.R.Neureuther and F.H.Dill, "photoresist Modeling and Device Fabrication Applications," optical and Acountical Micro-Electronics,polytechnic press,1974,pp.233-249.
- [11]. H.L.Stover,M.Nagler,I.Bol,and V.Miller, "Submicron optical Lithography:I-line Lens and photoresist Technology," optical Microlith.111,proc.,SPIE Vol.470,1984,PP.22-23.
- [12]. I.I.Bol, "High-Resolution optical Lithography using Dyed single-Layer Resist," Kodak Microelec. seminar interface,1984,pp.19-22.

- [13]. J.F.Bohland,H.F.Sandford and S.A.Fine,"Effects of Dye Additions on the Exposure and Development Characteristics of positive photoresists,"Advances Resist Tech.11,proc.,SPIE Vol. 539,1985,PP.267-274.
- [14]. A.V.Brown and W.H. Arnold,"optimization of Resist optical Density for High Resolution Lithography on Reflective substrates,"Advances Resist Tech.11,Proc.,SPIE., vol.539,1985, pp.259-266.
- [15]. T.R.Rampalone and F.A. kuyan,"Improving Linewidth control over Reflective surfaces vsing Heavily Dyed Resists,"J.Electrochem. soc.,vol.133,No.1,1986,pp.192-196,and Kodak Microelce. Seminer interface,1985.