Chimia 48 (1994) 431–432
ISSN 0009–4293

Microlithographic Layers

Ulrich Schaedeli* and **Eric Tinguely**

Abstract. Microlithography is a highly precise pattern-transfer technique, needed for the manufacturing of semiconductor devices. In the microlithographic process, the image of a mask is transferred to a light-sensitive polymer film, a so-called photoresist. Photoresists consist of light-sensitive organic polymers, which are able to resolve submicrometer patterns. They are highly specified materials, having well-defined physical and mechanical properties, and are mainly composed of a linear organic polymer, a photoacid generator, and a solvent.

1. Introduction

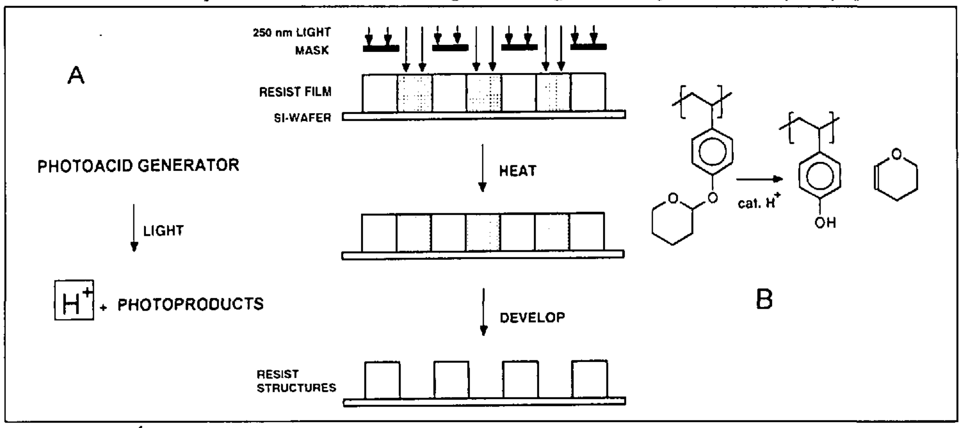
There has been a steady trend towards an ever increasing miniaturization and performance gain of electronic devices during the last two decades, which seems to continue until the end of this century, at least. The integrated circuit (IC) is located in the centerpoint of this development. Since the complexity of ICs is steadily increasing, new applications for semiconductor devices are becoming possible. This gain in performance of IC devices is made possible by densifying the network of active functions (transistors, diodes) on the same piece of monocrystallin silicon (chip). Whereas in 1965, a maximal amount of 250 electronic functions could be mounted on a silicon chip with the size of a fingernail (1 cm^2), this number rised during the eighties to more than a million. Today, state-of-the-art devices can house up to 100 millions of electronic functions. It is believed that memory devices with the ability to store 1 Gbit of information, or even more, will turn into reality at the beginning of the next century. The area of a chip has not been changed a lot along the evolutionary pathway and has stayed at about fingernail size. However, the size of the active components of a chip has decreased from 20 μm (1 micron = 1μm = 1/1000 mm = 10^{-6} m) in 1963 to 2 μm in 1983 and lies currently at around 1/3 μm (= 330 nm = 3300 Å).

The three-dimensional electronic functions of an active IC device are manufactured by a sequence of lithographic steps. This reproductive technique is called microlithography and allows for the highly precise transfer of submicron patterns from a mask to a light-sensitive polymer film, a resist [1][2]. It is not easy to visualize the smallness of submicron dimensions, but microlithography would allow for the generation of dozens of ordered structures on the dimension of a human hair with a diameter of 50 μm. The pattern of the structured resist is finally transferred by etching methods to the underlying semiconductor substrate. For the build-up of a working IC device, this microlithographic pattern transfer process has to be repeated up to twenty times.

2. Resist Materials

Typically, a modern photoresist is composed of a linear organic polymer, a substance which generates strong *Brønsted* acid upon irradiation, and a solvent. Resist films of *ca.* 1 μm thickness are obtained by spin-coating of the photoresist solution onto the semiconductor substrate (wafer), followed by evaporation of the solvent. The reaction sequence outlined in the *Scheme* is involved in the image-forming process: in a first step *A*, acid is formed in the irradiated zones of the resist film. In a

Scheme. *Reaction Sequence Involved in the Image-Forming Process of a Chemically Amplified Resist*



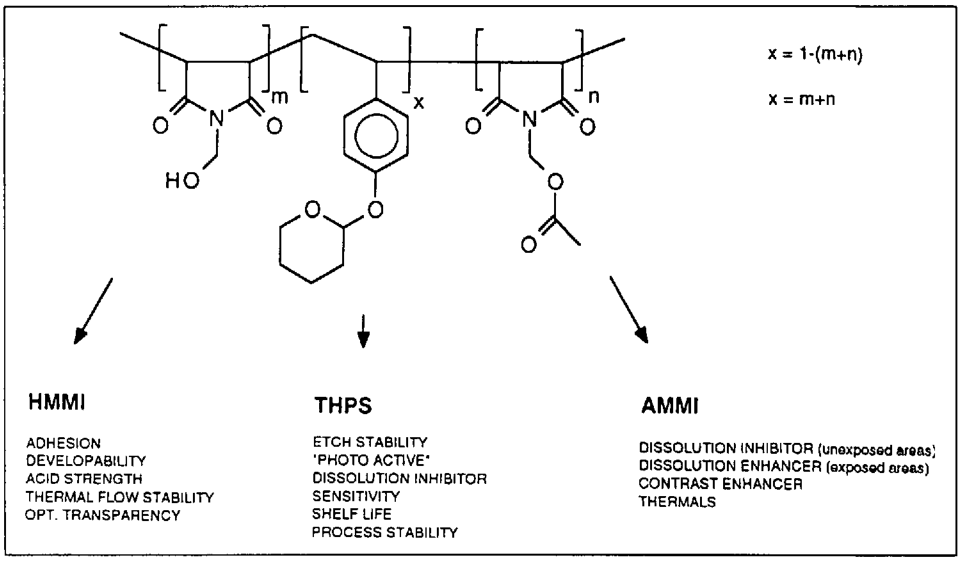


Fig. 1. *Maleimide-based resist polymer*

**Correspondence*: Dr. U. Schaedeli
Ciba-Geigy AG
Research Center Marly
Materials Research
CH–1723 Marly

CHIMIA 48 (1994) Nr. 9 (September)

subsequent step *B*, the photogenerated protons are used to catalytically cleave the acid-labile tetrahydropyranyloxy blocking moiety linked to the polymer backbone. The net result is a big change in polarity between exposed and non-exposed zones of the resist film. This allows for the development of the deblocked, polar zones in aqueous alkaline solution. Since one proton can initiate a large number of chemical changes, chemical amplification [3–5] is achieved, leading to highly sensitive resist materials.

We have found that the desired properties are combined in new polymers consisting of maleimides and reversibly blocked *p*-hydroxystyrene [6]. Each of the three monomers is adding specific properties to the final resist (*Fig. 1*). Synthetic routes yielding the desired monomers were established, along with a polymerization method leading to polymers having the desired monomer built-in ratio and molecular weight distribution. Resist formulations were obtained by dissolving the polymers, along with triphenylsulfonium triflate (photoacid generator), in cyclohexanone. If the corresponding resist films were imaged at 250 nm, resolution below 1/4 micron was achieved (*Fig. 2*).

3. Perspectives

Microlithography is a valuable technique for the generation of small-size patterns. New resist materials, which can be imaged at shorter wavelength to allow ever better resolution, will be needed for the manufacturing of future generation ICs. Our goal is to provide our customers, manufacturers of microelectronic devices, with these materials. Therefore, a resist chemist's work has to start today, looking at new type materials, tailor-made for the shorter illumination wavelengths of the future. Furthermore, we are also looking at other applications, involving the need for highly specified photosensitive materials.

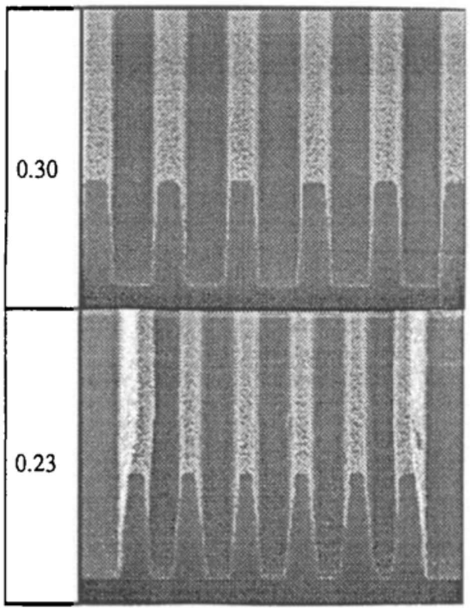


Fig. 2. *SEM Pictures of 0.23 μm and 0.30 μm line/space patterns in a resist based on maleimide polymers*

Received: July 7, 1994

[1] L.F. Thompson, C.G. Willson, M.J. Bowden, ACS Symposium Series, Vol. 219: Introduction to Microlithography: Theory, Materials, and Processing, 1983.
[2] A. Reiser, in 'Photoreactive Polymers, The Science and Technology of Resists', Wiley Interscience, New York, 1991.
[3] H. Ito, C.G. Willson, *Polym. Eng. Sci.* **1983**, *23*, 1012.
[4] J.M.J. Fréchet, E. Eichler, H. Ito, C.G. Willson, *Polymer* **1983**, *24*, 995.
[5] J.M.J. Fréchet, H. Ito, C.G. Willson, Proc. Microcircuit Eng. 260, Grenoble, France, 1982.
[6] U. Schaedeli, N. Münzel, H. Holzwarth, S.G. Slater, O. Nalamasu, *Proc. SPIE* **1994**, *2195*, 98.

Chimia 48 (1994) 432–435
ISSN 0009–4293

Colored Systems with Improved Weatherfastness

Laurent Chassot*

Abstract. Weatherfastness of pigmented organic coatings is a classical problem in the industrial world. We describe the photoreactivity of some heterocyclic pigments from the 1,4-dioxopyrrolo[3,4-*c*]pyrrole (DPP) family in suspension and in a polymer matrix, and the discovery of the photostabilization of organic crystals by nitroxy radicals.

1. Introduction

Pigments are finely divided, organic or inorganic, crystalline solids. They are used mainly for the coloration of polymeric materials like surface coatings (paints), plastics, synthetic fibers, and printing inks [1]. Contrary to dyeing, the coloration is obtained by dispersion of the microcrystals (0.01–1 μm) without dissolution of the chromophore molecules. Colored materials are made by purpose to absorb light, and it has been estimated that half of the annual production of polymers is employed outdoors [2]. Light stability is then a crucial property, because the consumer's interest is in having articles with long life expectancies. For example, the shade of an automotive coating has to be stable for more than four years. For the manufacturer, this means bringing systems onto the market which have better light and weather stability.

Photodegradation of systems containing inorganic pigments like TiO_2 is well documented [3]. However, the diversity of the photochemical processes underlying the degradation of organic pigments renders the field difficult and the literature covering the subject is scarce. Nevertheless the Pigment Division of *Ciba* started in its research center at Marly a project on colored systems with improved light- and weatherfastness [4].

2. Description of the Problem

A colored system has two major components, the pigment and the polymeric material (*Scheme*). Both of them will absorb part of the incoming light and partic-

**Correspondence*: Dr. L. Chassot
Ciba-Geigy Ltd.
Research Center Marly
Pigment Research
CH–1723 Marly