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New Materials by Photopolymerization

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Abstract. Despite lateral resolution being the most intensely studied topic in photopolymer research, vertical resolution properties finally add the decisive momentum to reach the desired performance in photopolymer layers. We will describe four different classes of industrial photopolymers on the basis of a light absorption and penetration model: microelectronic layers featuring submicron resolution, photopolymer materials for the manufacture of Printed Wiring Boards putting emphasis on chemical and mechanical stability of the permanent layers, three-dimensional stereolithography systems exhibiting tailor-made in-depth build-up of mechanical stability and thick-layer photolithography touching the centimeter-range.

1. Introduction

The major advantage of chemistry triggered by light undoubtedly lies in its ability to be switched on and off by light and shadow: so an image-forming process can be realized. Photosensitive polymer layers may, therefore, serve as photostructured masks for printing technologies whose commercial applications span from textile printing to microelectronic wafer processing. The major property of these layers – to resist to image fixation processes such as etching, galvanizing, sputtering, ion implanting or dyeing – made them a work-horse of the electronics, decorative and textile industry.

Efforts in sophisticated optics have been undertaken to approach lateral resolution to its physical limits. By means of phase-shifting masks [1] and off-axis illumination [2] the resolution of microphotoresists is reaching the dimensions of the incident exposure wavelength [3]. Despite the ongoing race for ultimate lateral resolution in the *x,y*-plane, the vertical resolution of photolithography systems is also playing an important role by adding the desired mechanical, electrical, and chemical properties to the imaged layer system. In short terms: it is this third dimension that converts a photopolymer layer really into a material.

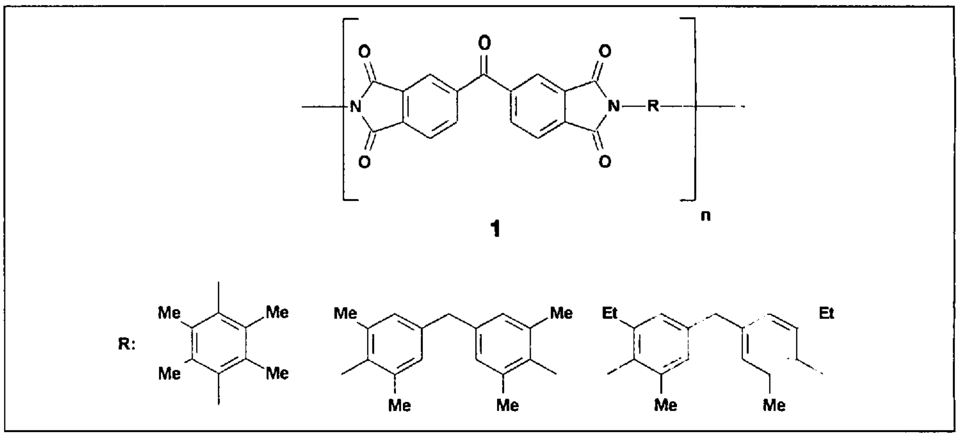
2. A Vertical Resolution Model

Vertical resolution follows the absorption laws of *Lambert-Beer* and, therefore, depends only on the extinction coefficient and the concentration of the light-absorbing species. Using *Lambert-Beer*'s law *Fig. 1* depicts the correlation between the molar extinction coefficient, and the depth light may penetrate into a material of 3 mol/l concentration, until it is absorbed to 90%.

It is noteworthy that vertical resolution may easily reach values of less than one tenth of the wavelength of incident light at very high extinction coefffcients – a value, which outpaces by far the capabilities of lateral resolution being strictly bound to restrictions stemming from the exposure wavelength and the numerical aperture of the optical system. Molar extinction coefficients below 0.01 mol^{-1} dm^2, on the other hand, allow light to penetrate several cm deep into the bulk of a photosensitive material. It is our aim to describe here photopolymer systems, technologies, and applications where the resolution in the *z*-axis has to be taken into consideration.

3. Microelectronic Layers

Permanent polymer layers in microelectronic devices have to withstand high temperatures, steep heat gradients and stress build-up. Polyimides are today's widely accepted materials in the manufacture of integrated circuits and multilayer interconnection systems [4]. Fully imidized solvent soluble polyimides **1** based on 3,3',4,4'-benzophenonetetracarboxylic anhydride and *ortho*-alkyl-substituted diamines can be directly photocrosslinked [5]: they exhibit photocrosslinking activity at 365-nm exposure wavelength and an excellent thermal stability up to 400°. The importance of light absorption in the layer is easily demonstrated by the considerable improvement effect in photospeed in **1**, if the benzophenone chromophore is partly replaced by the highly absorbing thioxanthone segment: substitution of 10 mol-% of the benzophenone units by thioxanthone results in a 2.5 fold increase in photocross-linking speed. Interference patterns on the side walls allow to extrapolate the lateral resolution potential and may raise the question: how does light travel trough this layer?



A further importance of through-layer light absorption manifests in the behavior of photosensitive polyimides and resists on reflecting, polished *vs.* dispersing, rough supporting surfaces. Whereas reflecting the light back from the planar surface just creates standing wave pattern in the photosensitive layer, light will scatter into all directions through a layer placed on a rough surface destroying the image resolution. Derived from inner filter effect considerations an optimum total optical density of 0.4343 of the layer has been calculated [6].

4. Photopolymers for the Printed Wiring Board

The manufacture of Printed Wiring Boards calls for permanent layers exhibiting good protection capabilities against

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hot liquid solder, dust, chemicals, and mechanical impact. Uniform material properties throughout the whole layer thickness (10-50 μ) are either achieved by a B-stageing process combining photolithographic definition of the image surface, dissolution of the photoinsolubilized structure, followed by an efficient thermal cross-linking step of the bulk or by an in-depth photopolymerization process, which ensures light penetration through the entire profile [7].

The absorption spectrum of such a resin/photoinitiator system changes with prolonged exposure as shown in *Fig. 2*. A photopolymer film composed of an epoxidized cresol novolak and (η^6-naphthalene)(η^5-cyclopentadiene)iron(II) hexafluorophosphate was irradiated for standard time intervals and the resulting spectral changes were registered. As can be seen, the optical density in the near UV and the visible part of the spectrum decreases with time showing a bleachable photoinitiator system that permits light penetration through thick layers. *Fig. 3* shows a scanning electron micrograph of such a film (thickness 100 μ) and its vertical wall profile indicating a high contrast.

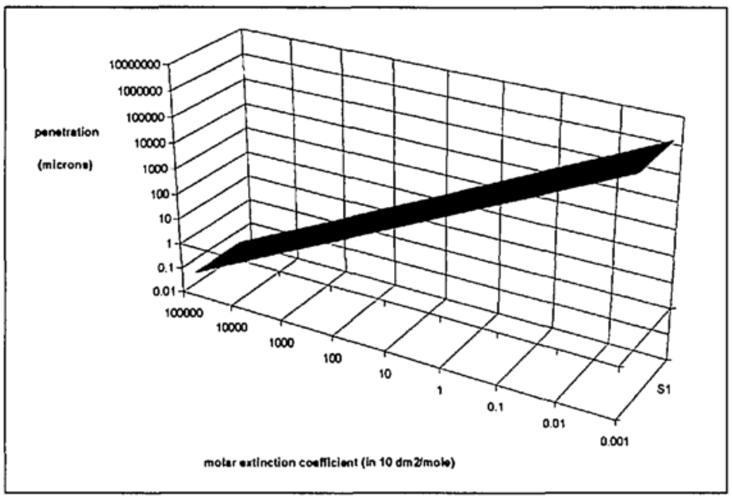

Fig. 1. *Penetration of light into a layer containing 3 mol/l of a chromophore in relation with its molar extinction coefficient*

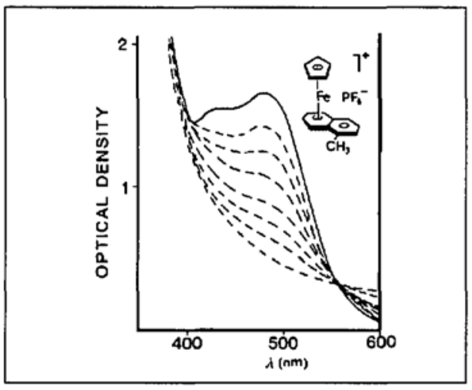

Fig. 2. *Changes in the UV/VIS spectrum of a photopolymer film* (ECN 1299, 2.5% (*w/w*) (η^6-naphthalene)(η^5-cyclopentadiene)iron(II) hexafluorophosphate) *by irradiation*. Time interval: 10 s [7].

Fig. 3. *Scanning electron micrograph of UV exposed ECN 1299/iron-arene initiator photoresist.* The vertical wall profiles are indicative of high contrast. Film thickness: 100 μ [7].

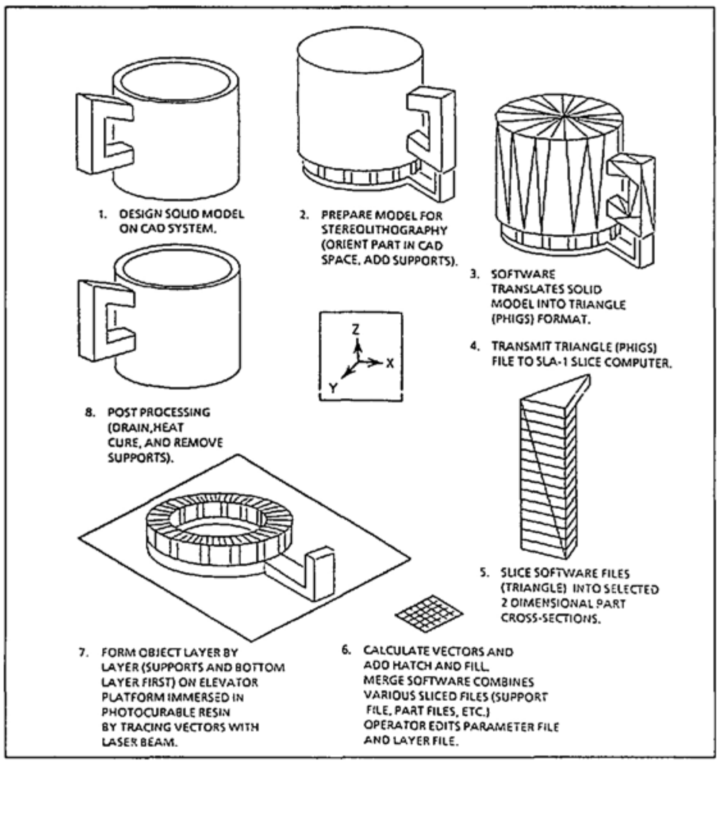

Fig. 4. *Key steps in the stereolithography process* [14]

5. Stacked Lithographic Layers: Stereolithography

In 3D-stereolithography the problem of light penetration into thick resin layers (0.1 mm and more) has been turned into a virtue: with the help of laser-induced photopolymerization of a liquid acrylate/photoinitiator formulation carefully tuned to optimum in-depth light absorption a sequential build-up of demanding three-dimensional structures has been realized [8]. *Fig. 4* describes the key steps of this technology:

- a solid CAD model is sliced into cross-sections by a software translation and reinforced by hatches
- the object is then formed in a layer-by-layer photoprocess on a vertically movable platform immersed in the photocurable liquid resin vat by tracing vectors with a laser beam
- a post-cure exposure in the bulk assures the desired final material properties.

The build-up of mechanical properties (modulus, strain, impact strength and hardness) depends on the combination of monomers and radical photoinitiators and on the cross-section design. Holographic cure monitoring [9] and Photo-Differential Scanning Calorimetry are powerful means to follow this reaction.

In *Fig. 5*, representing the build-up of relative *Young*'s modulus of a acrylate resin/radical photoinitiator formulation with respect to the exposure energy, two zones of photoresponse can be differentiated: at low exposure energies (up to 10 times the critical energy E_c being defined as the energy needed to get gelation of the resin) a linear relationship has been found. This is the typical working energy range for stereolithographic build-up of three-dimensional shapes with sufficient green

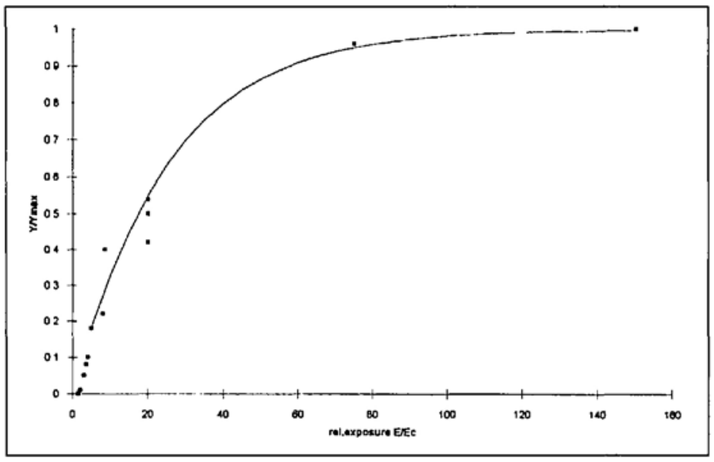

Fig. 5. *Build-up of relative* Young*'s modulus* (Y/Y_{max}) *with increasing relative exposure energy* (E/E_c)

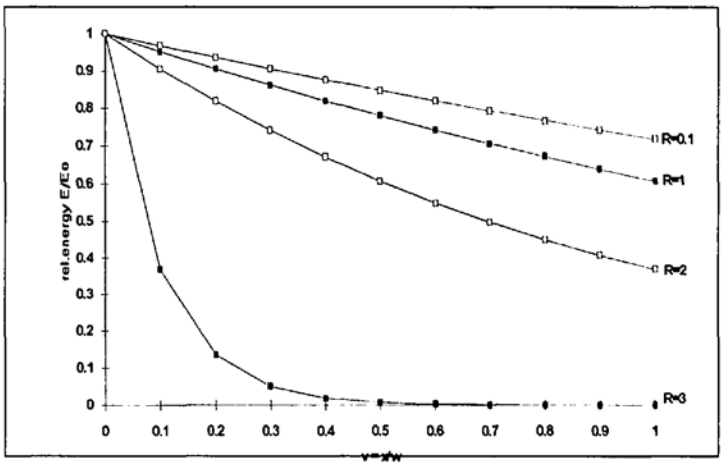

Fig. 6. *Penetration* v *of relative light energy* E/E_o *into a layer of thickness* w *featuring different light penetration depths* R

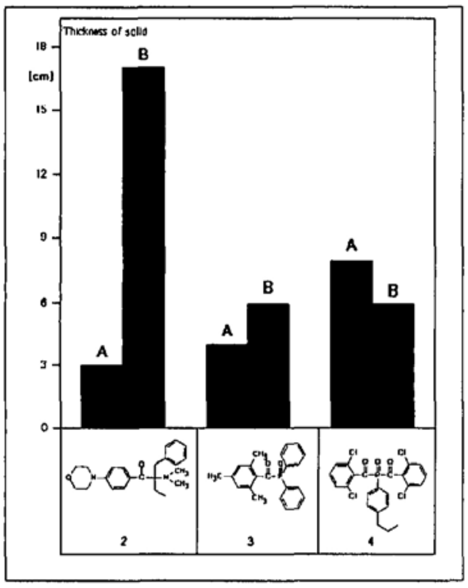

Fig. 7. *UV Curing of thick sections of acrylate mixtures containing 0.1 mol-% of photoinitiators* **2**, **3**, **4**. Formulation *A*: 70% prepolymer, 30% hexanediole diacrylate. Formulation *B*: prepolymer replaced by an aliphatic urethane acrylate.

Table. *Lateral and Vertical Resolution in Optical Lithography*

Properties	Lateral resolution	Vertical resolution[a])
maximum resolution	order of wavelength	1/10 of wavelength
aspect ratio (thickness/resolution)	> 5, normally 1–3	unlimited
wavelength dependence of resolution	improves with shorter wavelength	best at highest absorption wavelength of material
industrial applications	Photoimaging in textile, electronics, decorative industries	3D-Stereolithography, printing plates, permanent layers in electronics

[a]) Vertical resolution helps photopolymer materials to fulfil tasks exceeding imaging and masking. Such systems might be used for lithographic microfabrication of micromechanical devices in the submicron range, *e.g.* gears, motors, and switches using microplastic photopolymer structures [13].

strength. Flood post-exposure finalizes the cure and assures the desired mechanical bulk properties. Here the linear dependence of modulus gain *vs.* exposure energy levels off towards an asymptotic value. It is obvious that the profile of the individual slices always exhibits an exponential response in their vertical direction paralleling light absorption, due to the law of *Lambert-Beer*. *Fig. 6* depicts the relative portion E/E_0 of light absorbed in a layer of thickness *w*, when exposed to light of energy E_0. If the penetration depth D_p (defined as that path length of resin that will reduce the exposure, at the wavelength considered, to l/*e* of the surface exposure) is very big compared to the thickness ($R = w/D_p = 0.1$) light will fully penetrate, but if D_p is one third of the thickness ($R = 3$), considerable absorption takes place and the modulus gain will be highest at the top of the irradiated slice and lowest at its bottom [10].

6. Thick-Layer Photolithography

In the printing industry photopolymer layers of 0.5 mm serve as base material for newspaper printing plates [11]. It is a prerequisite for the efficiency of this photolithographic process that the photoinitiators have weak absorption bands, low laying triplet states and all efficient photobleaching mechanism (*Fig. 7*).

Where is the upper limit of thickness? A photo-casting system of liquid acrylates and radical photoinitiators has been shown to cure layers up to 25 cm [12].

7. Summary and Outlook

The lateral and vertical resolutions in optical lithography are given by two different physical limits: the lateral resolution is determined by the quality of the incident light beam, its wavelength and diffusion phenomena in the lithographic layer. The vertical resolution, however, depends entirely on a genuine material property: the absorption coefficient of the chromophore and its change during irradiation (see the *Table*).

[1] M.D. Levenson, *Microlithography World*, March/April 6, 1992.
[2] N. Shiraishi, S. Hirukawa, Y. Takeuchi, N. Magome, *Microlithography World*, July/August 7, 1992.
[3] S. Uchino, T. Tanaka, T. Ueno, T. Iwayanagi, N. Hayashi, *J. Photopolym. Sci. Technol.* **1992**, *5*, 93.
[4] P. Burggraaf, *Semiconductor Int.* **1988**, *11*, 18.
[5] O. Rohde, P. Smolka, P.A. Falcigno, J. Pfeiffer, *Polym. Eng. Sci.* **1986**, *32*, 1623.
[6] A.R. Gutiérrez, R.J. Cox, *Polym. Photochem.* **1986**, *7*, 517.
[7] K. Meier, H. Zweifel, *J. Imaging Sci.* **1985**, *30*, 174.
[8] US Pat. 4 575 330 (*3D-Systems Inc.*, Valencia, CA), 8.8.1985.
[9] P. Bernhard, M. Hofmann, M. Hunziker, Proceedings of 2nd Conference on Rapid Prototyping, Daytona, 1991, p. 86.
[10] B. Evans, P. Jacobs, Proceedings of 2nd Conference on Rapid Prototyping, Daytona, 1991, p. 69.
[11] W. Rutsch, Proceedings of the XVIth International Conference in Organic Coating Science and Technology 1990, p. 423.
[12] S. Ozaki, K. Naguchi, Proceedings of RADTECH Asia 1991, p. 208.
[13] W.E. Feely, Proceedings III of Advances in Resist Technology 1986, SPIE No. 631, p. 48.
[14] Courtesy of *3D-Systems Inc.*, Valencia, CA.