

INORGANIC-ORGANIC COMPOSITES (ORMOCERS) AS STRUCTURED LAYERS FOR MICROELECTRONICS

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ABSTRACT

Enhanced integration, faster signal transmission and reduced size of mounting devices in components for microelectronics requires new patternable materials. Inorganic-organic copolymers (ORMOCERS = ORganically MODified CERamics), prepared by sol-gel techniques have been developed for interconnection technologies in microelectronics. Photopolymerization is enabled by unsaturated hydrocarbon or epoxide substituents and UV-sensitive initiators. Using a frequency doubled Argon-ion laser at 257 nm for direct laser writing, patterned layers with high edge quality have been realized. In combination with high breakthrough voltages, low permittivity constants and high bulk resistivities they open interesting aspects for very large system integration techniques (VLSI).

INTRODUCTION

The potential of new generations of ram and rom chips, especially processors, cannot be fully utilized without enhanced integration and multilayer technology [1]. Therefore microelectronics requires tailor-made materials and new techniques for interconnection. Multilayer technology demands patternable dielectric materials with especially high electrical resistivity for high density of conducting paths, low permittivity constants for minimum signal deformation and good adhesion to substrate material and to active and passive components.

At the present state of the art dielectric materials like polyimide or polyimide/polyamide blends are well established [2]. For higher integration, however, the permittivity constant should be as low as possible, and water take up has to be minimized. As shown in [3], ORMOCERS could be synthesized with low ϵ values, good adhesion to substrates like aluminum, extremely low H₂O take up and curing temperatures as low as 280 °C. In [4] the possibility of the development of photolithographic patterns was investigated and it was shown, that ORMOCERS with polymerizable groups can be patterned. The objective of the present investigation was to develop ORMOCERS able to be patterned by direct laser writing techniques. This technique provides a flexible tool for microelectronic design. Therefore several types of ORMOCERS have been synthesized and tested for direct laser writing.

EXPERIMENTAL

Three compositions have been developed:

I: 0.45 mol 3-methacryloxypropyltrimethoxysilane, 0.30 mol phenyltrimethoxysilane, 0.25 mol aluminiumtri-sec.-butylate

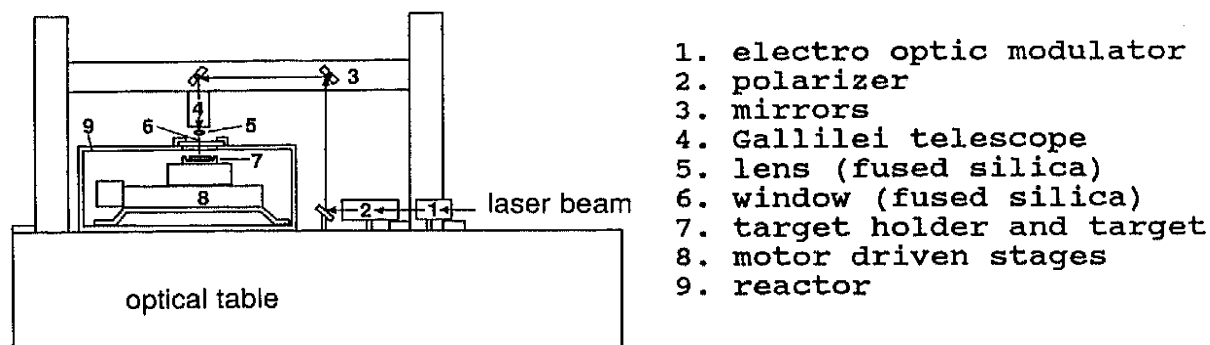
II: 0.39 mol 3-(glycidoxypropyl)trimethoxysilane, 0.39 mol 3-methacryloxypropyltrimethoxysilane, 0.18 mol vinyltrimethoxysilane, 0.04 mol tetraethoxysilane.

III: 0.39 mol 3-(glycidoxypropyl)trimethoxysilane, 0.39 mol 3-methacryloxypropyltrimethoxysilane, 0.18 mol diphenylsilanediol, 0.04 mol tetraethoxysilane.

The components were mixed together without solvent and refluxed under air up to 6 hours. 50 % of the water necessary for a stoichiometric hydrolysis was added successively. The clear, viscous liquid was cooled to room temperature and stored in closed bottles.

For coatings, IRGACURE* 184 (photo initiator from Ciba Geigy) is added and the materials are applied onto the substrates (glass, silicon or thin film quality Al_2O_3) by spin coating and a coating thickness of 10 μm is obtained. Before photo curing, the coatings were dried at room temperature for 30 min. Photo curing can be carried out by UV radiation (1000 W high pressure mercury lamp) or by using a frequency doubled Ar ion laser (for patterning). After polymerization, the final curing has to take place at $T > 120$ °C for one hour. Patterned samples are developed before post baking with acetone/ultrasonic treatment. System II can be developed with 0.1 N NaOH within 10 seconds, too.

For laser writing a frequency doubled Ar ion laser yielding up to 100 mW at 257 nm was used.



1. electro optic modulator
2. polarizer
3. mirrors
4. Gallilei telescope
5. lens (fused silica)
6. window (fused silica)
7. target holder and target
8. motor driven stages
9. reactor

Figure 1: Scheme of the laser writing equipment

The set up is shown in fig. 1. The laser beam is directed towards the horizontal target via several mirrors. To achieve a minimum laser spot size the beam passes through a gallilean telescope expanding the beam by a factor of 2. A mechanical shutter or an electro optic modulator are used to turn the beam on and off by computer control. Finally the laser beam is focused by a quartz lens onto the target. The target itself is placed onto two motor driven stages providing the horizontal xy-movement. To adjust the focus on the target the lens position can be varied. The positioning system can be placed completely inside a vacuum vessel to operate under oxygene free conditions. To achieve the required flexibility in creating various patterns the positioning

system as well as the lens position are controlled by a computer. The resolution of the system is 100 nm at a maximum velocity of 20 mm/s.

For controlling focus diameter and profile the laser spot radius is measured using the scanning knife edge method [5]. A razor blade is placed on the target and while scanning the edge through the laser spot the intensity is monitored. The laser spot diameter is determined by differentiating the intensity profile. So far the smallest spot size thus obtained is 8 μm .

The kinematic viscosity of the ORMOCER lacquors has been measured by Ubbelohde method. Kinetic measurements have been performed by IR transmission spectroscopy of ORMOCER coated silicon wafers. Adhesion is tested by grid test (DIN 53151) combined with tape test. Shape and quality of the structures are documented by scanning electron microscopy and profilometric measurements. The thermochemical behaviour is investigated by DTA and TGA coupled with mass spectroscopy (TGA-MS) using a heating rate of 10 K/min. Dielectric strength is measured using an ORMOCER coated metal substrate and a metal brush as counter electrode. Permittivity constant and bulk resistivity are measured using a 10 KHz ac voltage. A humidity test was carried out according to DIN 50017, where ORMOCER coated substrates have been exposed to 100 % rel. humidity at 40 °C for 14 days. Subsequently the adhesion and the quality of the coating have been checked visually by polarized light microscopy.

RESULTS AND DISCUSSION

General material properties

For the applicability of coating systems, their viscosity and their shelf life is important. The kinematic viscosities of all three systems are in the range of $< 10^{-5} \text{ m}^2/\text{s}$ after synthesis and it is possible to obtain coating thicknesses of about 10 μm with very good surface qualities. System I shows a sharp rise in viscosity after three days storage. The viscosity/storage time dependence for system II is given in fig. 2. System III has a shelf life around three months. That means that system II is the most suitable system for carrying out coating experiments from the same batch and therefore, this system was chosen for the majority of the laser writing experimental investigations.

The comparison of the adhesion of the three systems is given in table 1.

Table 1 Adhesion of the ORMOCER systems

Substrate material	system I	system II	system III
aluminumoxide ceramic	0-1	0-1 (200°C)	0-1 (260°C)
glass	0-1 (150°C)	3-4	1-2
silicon wafer	1-2	2-3	1-2

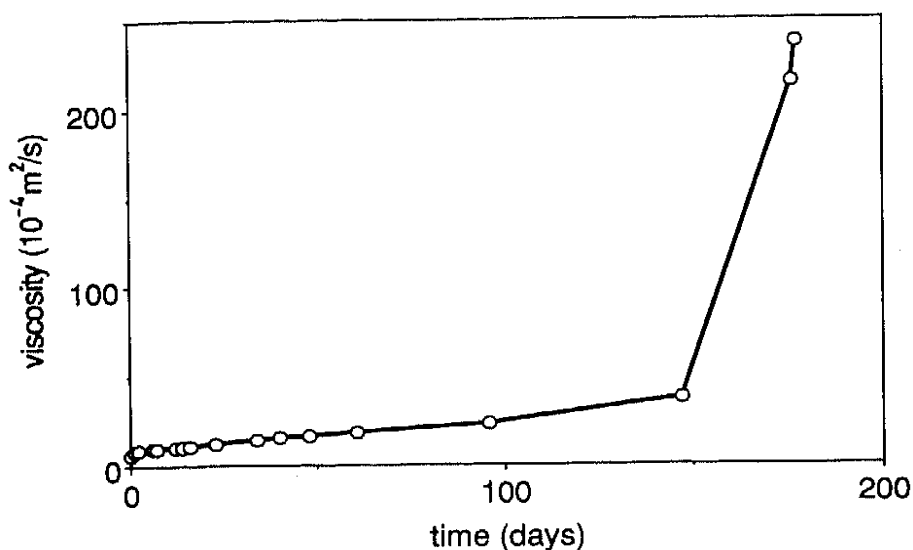


Figure 2: Time dependence of viscosity of system II.

In this test 0 corresponds to very good adhesion while 5 indicates no adhesion at all. Values in brackets indicate the temperature for the beginning of a reduced adhesion. All systems show very good adhesion to aluminumoxide ceramic. Only a poor adhesion to glass and silicon is found for system II. System III exhibits good adhesion on aluminumoxide ceramic even at high temperatures.

TGA-MS analysis shows the beginning of decomposition at $T > 200$ °C for system II and $T > 270$ °C for system III. Thus system III fulfills the temperature requirements imposed by the soldering process.

All systems passed the humidity resistance test according to DIN 50017. Furthermore all systems are resistant to organic solvents like alcohols and acetone for at least a few minutes. Long time immersion of system III in acetone causes only a weight loss less than 0,5%.

The electrical properties have been determined for system II and III. They both show a bulk resistivity larger than $10^{14} \Omega \cdot \text{cm}$ and low permittivity constants depending on sample preparation and curing history. The permittivity constants are varying between 3 and 6, but at the moment for both systems there cannot be given clear dependencies. The dielectric strengths for systems II and III are determined (100 V/ μm for system II and 400 V/ μm for system III).

UV-curing of ORMOCERS

The behavior was investigated for system I. It is similar to the polymerization of MMA. In fig. 3 the decay of the C = C bond concentration, measured by IR, of the methacryl groups of system I is shown. As one can see, about 20 % of the C = C bonds remain unreacted, probably due to the increa-

sing stiffness of the network due to polymerization. The effect on the long term stability of the olefinic residual groups has to be investigated.

For laser writing experiments, system II was coated onto glass, silicon and Al_2O_3 substrates. During the curing step at 120°C , a substantial reduction of SiOH groups occurs, which could be followed by IR spectroscopy. A shrinkage of about 5 % by volume takes place.

The performance of the patterned layer depends on the material properties, the polymerization conditions (mainly

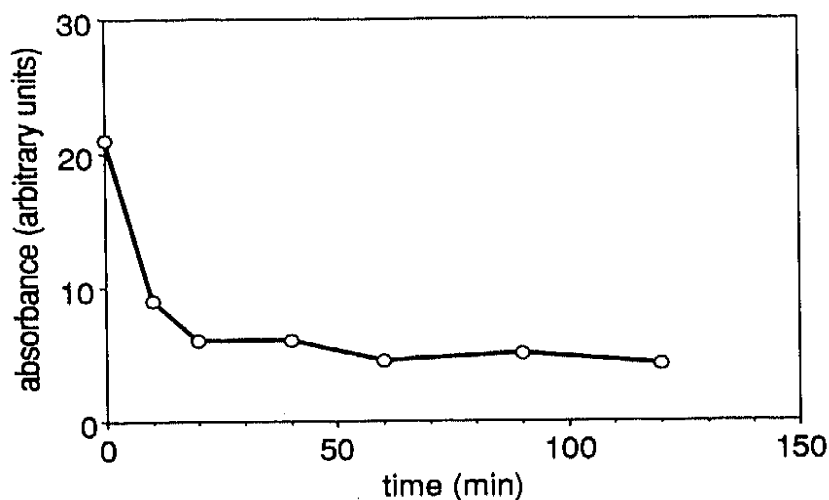


Figure 3: Time dependent absorbance of $\text{C}_2=\text{C}$ vibration at 1630 cm^{-1} (Hg low pressure lamp, 3 mW/cm^2 , 2 mass% IRGACURE* 184)

the laser parameters and the initiator) and the development conditions. Of special interest are parameters like laser beam intensity and initiator concentration. For laser polymerization radiation density, adsorption of the matrix, radiation time, quantum yield, radical yield and lifetime are the important parameters. It is extremely difficult to estimate these parameters in a laser scanning process, and furthermore, there is a high probability of uncontrolled polymerization by scattered light or reflected light from the substrate surface. Therefore it is necessary to control the width of the patterns as a function of processing parameters. In fig. 4, the dependence of width of the structure on laser beam intensity is shown. One can see a broadening of the width of the structure in rising the laser intensity. Increasing the initiator concentration at higher laser power causes more drastic broadening.

Fig. 5 shows the log dependence of the width on the initiator concentration for a laser intensity of 0.7 mW and 2.1 mW . The influence of the laser intensity on structure broadening seems to be lower compared to the initiator influence.

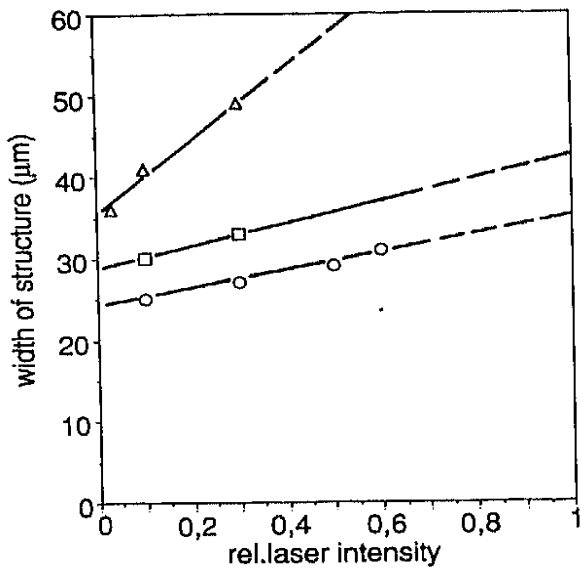


Figure 4: Dependence of width of structure on laser beam intensity
 -○ 0.05 mass% initiator
 -□ 0.1 mass% initiator
 -△ 1.0 mass% initiator

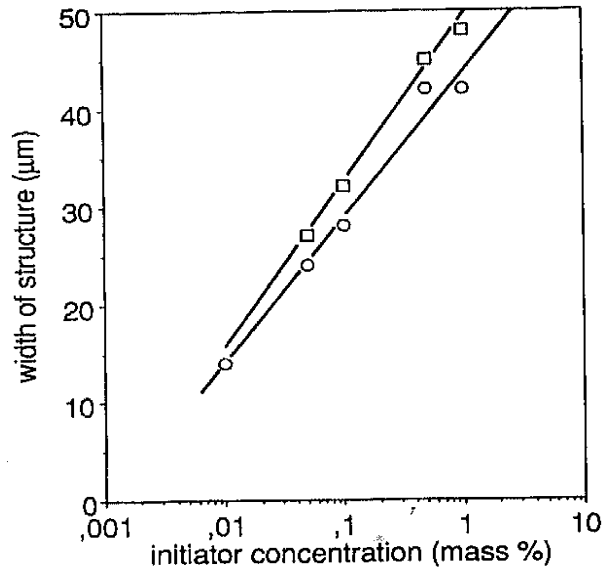


Figure 5: Dependence of width of structure on initiator concentrations
 -○ at 0.7 mW
 -□ at 2.1 mW

An incomplete polymerization process will cause structures containing reaction time dependent concentrations of oligomers soluble in developing processing solvents. Elution of these oligomers will cause a shrinkage of structure in height and width. This effect is severe at low initiator concentration as shown in fig. 6 (initiator concentration: 0.01 wt.%).

Fig. 7 verifies good structure quality at optimized processing conditions (system II, $I_0 = 120 \text{ W/cm}^2$, stepping rate around 20 mm/s and $[I] = 0,2 \text{ wt.}\%$). The broadening of the structures from a laser spot size of 8 μm in diameter results in a width of 15 μm .

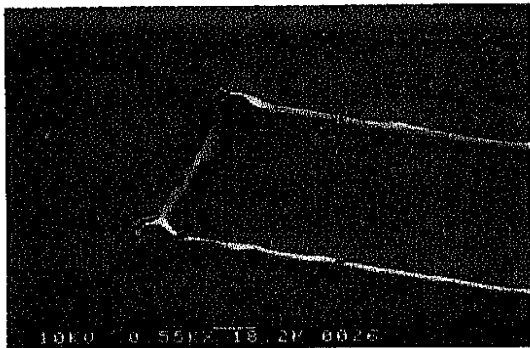


Figure 6: Patterned system II at initiator concentration of 0.01 wt.%.

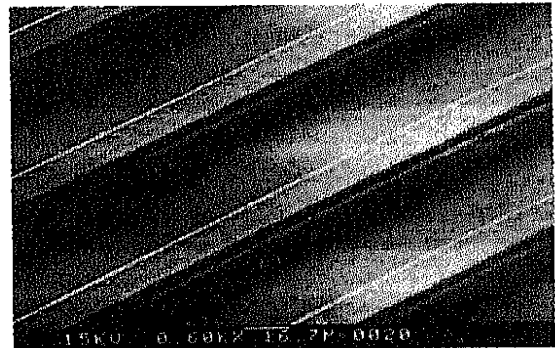


Figure 7: Patterned system II at more optimized processing

CONCLUSIONS

ORMOCERS are patternable by UV-radiation and UV-sensitive initiators. A process to pattern ORMOCERS via laser direct writing could be established. First experiments show very interesting material data and good quality of structure. Further investigation of the correlations between system composition, exposure to UV-radiation for polymerization and etching process have to be carried out to optimize patternable ORMOCER layers for electronic applications.

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