POLYIMIDE RESIN CURING IN MICROELECTRONIC APPLICATIONS

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KEYWORDS: microelectronics, resins, polymide resins, polymerizartion temperature, film quality, thin films, film degradation, film curing

ABSTRACT: Curing cycles of polyimide resins may be tailored to a specific microelectronics application, and polymerization times shortened without compromising the quality of the resulting film. However, curing these resins below 300°C may prevent full imidization and degrade the film.

Termična obdelava poliimidnih umetnih smol za uporabo v mikroelektronskih tehnologijah

KLJUČNE BESEDE: mikroelektronika, smole umetne, smole poliimidne, temperatura polimerizacije, kakovost plasti, plasti tanke, degradacija plasti, vulkanizacija plasti

POVZETEK: Termično obdelavo poliimidnih umetnih smol, ki jih uporabljajo v mikroelektronskih tehnologijah, je moč prilagoditi neki specifični uporabi. Vendar pa polimerizacija ne sme potekati pri temperaturah pod 300°C, ker sicer reakcija ne steče do kraja in kvaliteta takih polimernih tankih plasti je slaba.

1. Introduction

The polyimide group of cross linkable polymers has been investigated extensively in recent years, and successfully applied as planarization layers, intermetal dielectrics, passivation films, alpha particle barriers, adhesives, etc. in integrated as well as hybrid circuit technologies /1,2/.

Photosensitive polyimide resins have considerably increased the number of different applications of these materials /3/. The use of polyimide resins is primarily justified by its superior chemical and physical properties when cured, by its compatibility with many of the materials used in hybrid and integrated circuit technologies, and ease of their application which is similar to photoresist processing, including the required deposition and curing equipment.

Some of the drawbacks of the polyimide resins, their relatively short shelf life and gelled in time which influences their viscosity stability, can be bypassed by good housekeeping and are usually of little concern in a production environment.

Polyimide processing is relatively simple, convenient and adaptable. However, with respect to times and temperatures used in a curing cycle, there are restrictions which have to be observed when designing a curing schedule for a specific application. IR spectroscopy is a convenient tool for studying the state of polymerization of these resins /8, 9/, and a study of polyimide polymerization by this method is presented. (Results of this study have been previously published /8/.)

2. Materials and methods

The polyimide resin used in this work was Hitachi Chemical Co. PIQ (polyimide isoindoloquinazolinedione). The viscosity of the uncured resin is 1130 cps at 23°C. To facilitate spin coating the resin has been diluted with DMSO (4 parts resin to 1 part solvent). No adhesion promoter was used, even though in IC applications its use seems to be necessary /11/. Silicon wafers were coated with 2 successive coats of polyimide resin, resulting in a 2.0 μm thick film. The first coat was applied at 3000 RPM (30 sec) and dried at a 85°C for 30 min. to remove the solvents. The second coat was then applied and the resulting polyimide film cured. The two step coating cycle has been used in order to obtain a uniform film thick enough to yield IR spectra with an adequate signal to noise ratio (100 : 1 in fully cured films). The IR spectrometer used is a Perkin Elmer Model 783, operated in the transmission mode.

The curing cycle recommended by the vendor of the resin is comprised of consecutive bakings at 100°C, 220°C, and 350°C for 1 hour each, in air ambient /4/. This is similar to the curing schemes for other polyimide products /1/.

The intensity of the imide bond absorption line at 1377 cm^{-1} /5/ was measured after the curing of the resin. No increase of the line intensity could be observed by increasing the duration and temperature of the recommended curing cycle, and therefore a sample cured as described above was considered to be fully cured.

The degree of polymerization of a partially cured resin was obtained by measuring the intensity of the imide absorption line, relative to the intensity of the line in a fully cured resin.

3. Results and discussion

Time dependence of the degree of imidization during curing at 200°C and 300°C is shown on Fig. 1. It can be observed that at 300°C the resin is fully cured already after 20 min. of curing time, without any previous baking at a lower temperature. Obviously the recommended curing cycle is set quite conservatively and can be shortened without compromising the degree of polymerization of the polyimide film.

Curing the polyimide film even for extended periods at 200°C will not cause it to polymerize fully. Subsequent

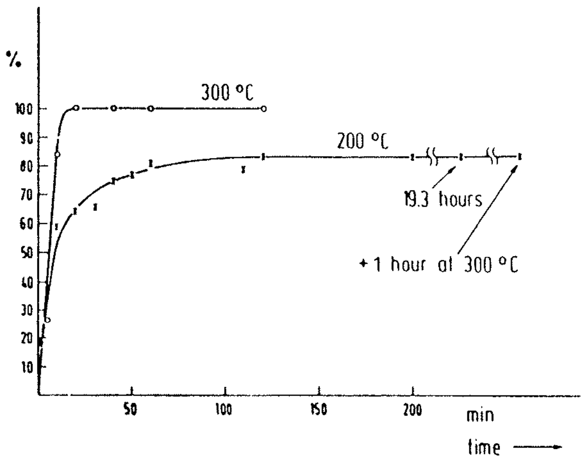

Fig. 1: Dependendence of the degree of imidization (in %) on curing time at 200 deg. C and 300 deg.C. After 19.3 hours at 200 deg. C the sample was baked at 300 deg. C for one hour.

curing of the resin at 300°C, after it has been exposed to 200°C for 20 hours, does not increase its degree of imidization. This indicates that prolonged exposure of uncured polyimide films to temperatures below 300°C will inhibit complete curing of the films, thereby degrading their properties. This incomplete curing may be a solvent effect, as described in literature /10/. In particular, the otherwise excellent scratch resistance of the polyimide passivation films seems to be much reduced by incomplete curing.

The activation energy of polymerization of the polyimide resin is 70 kJ/mole, as calculated from the data in Fig. 1. This value is on the high side of the range of the activation energies of similar polymers /6,7/.

Temperature dependence of the degree of imidization is shown on Fig. 2. Uncured films of polyimide resin were baked for 1 hour at a certain temperature, and the degree of imidization relative to the fully cured film measured. As above, the degree of imidization at 200°C remains limited, even after 20 hours baking time, and the film will not cure fully under subsequent exposure to 300°C. However, in films cured at 100°C subsequent high temperature curing will somewhat increase the degree of imidization.

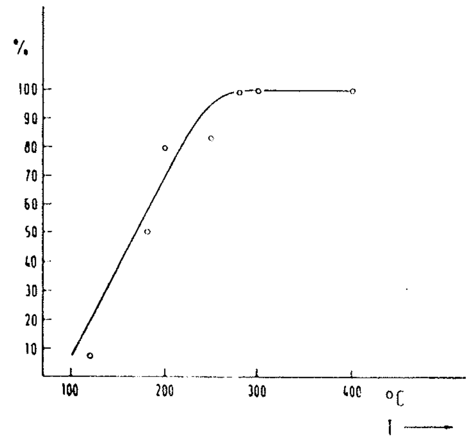

Fig. 2: Temperature dependence of the degree of imidization (in %) after 1 hour of curing time.

4. Conclusion

The standard curing schedule of the polyimide resin offers some latitude with respect to the reduced baking times. This is not true for the curing temperatures - extended exposures of the uncured resin films to temperature below 300°C will prevent full imidization of the material, thereby considerably reducing the properties of the polyimide films. This has to be taken into the account when designing a curing schedule for a specific application.

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