Positive Photosensitive Polyimide Having Long Term Heat Stability

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1. Introduction

Positive tone Photosensitive polyimide was widely used as protection layer, interlayer dielectrics, re-distribution layer for semiconductor devices [1]. To save energy consumption, inverter technologies are paying attention. Power devices such as power MOS-FET, IGBTs are indispensable for the inverter. Those power devices are required to operate high temperature (such as 150°C or high) for long time. Protective coatings for the power devices are required for long term heat stability. In this paper we report the positive photosensitive polyimide having long term heat stability.

2. Experimental

Polyimide precursors were prepared by following method. Poly(amic acid was obtained by addition of dianhydrides to diamines N-methyl-2-pyrrolidone (NMP, Mitsubishi Chemical) solution at 40°C for 4hrs under nitrogen flow. After obtaing the poly(amic acid), fixed amount of dried dimethylformamide diethyl acetal (DFA, Tokyo Kasei) was dropwised to the poly(amic acid) solution. The reaction mixture was stirring for 4hrs at 50°C under nitrogen flow. Equal amount of acetic acid to DFA was added to the solution at room temperature to decompose the redundant DFA. The solution was poured into water to obtain partial esterified poly(amic acid). The generated precipitate was filtered and washed water for several times. The obtained partial esterified poly(amic acid) was dried in a convection over for 72hrs at 80°C.

Photosensitive polyimide varnish was obtained by following method. Fixed amount of partial esterified poly(amic acid), photo active compound (Toyo Gosei), other compounds such as cross-linker were mixed and dissolved into gamma-butyrolactone (Mitsubishi Chemical) at 40wt% concentration. The photosensitive varnish was filtered by 0.5 μm polyfluorocarbon filter.

The obtained photosensitive varnish was coated on a 150mm Si wafer (E&M) at about 10um after 120°C soft baking by Mark-7 (Tokyo Electron). The coated wafer was exposed by i-line stepper (GCA, DSW-8750) at 0-1000mJ/cm². The exposed wafer was developed in 2.38% TMAH solution (ELM-D, Mitsubishi Gas Chemical) by Mark-7.

The developed wafer was cured at fixed condition to convert polyimide by an inert oven (CLH-21, Koyo Thermo System) under nitrogen.

The cured wafer was treated at 200°C for 2000hrs by convection oven (Tabai).

Polyimide thickness was measured by lambda ace (Dainippon Screen) after soft baking, after developing and after cure.

Cured polyimide film was obtained by following method. The cured polyimide wafer was immersed into 45% HF solution (Morita Chemical) for 10min at room temperature to remove from Si wafer. The peeled polyimide film was washed by water carefully for 10min. The obtained polyimide film was dried at 80°C oven (Tabai) for 1 night. The dried polyimide film was cut at 1cm width. Mechanical properties were obtained by RTM-100 (Orientech). Glass transition temperature was measured by DSC method (DSC-50, Shimadzu). Thermal decomposition was investigated by TG-50 (Shimadzu). All chemical structures using in this work was summarized in Fig. 1.
3. Results and discussion

Oxydianiline (ODA, Wakayama-Seika) and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropene (6FAP, AZ materials) are used as diamines. Molar ration of ODA and 6FAP is 1:1. 3,3',4,4'-tetracarboxylic diphenylether dianhydride (ODPA, Manac) was used as a dianhydride for reference polyimide structure for this study. Polyimide precursor for positive photosensitive polyimide was obtained by partial esterification reaction [2].

In order to achieve good photo-lithographic performance, molecular weight of polyimide precursor is about 10K (Mn). So molar ratio of diamine and dianhydride is 0.9. 3-Aminophenol (AP, Tokyo-Kasei) was used as a terminator. Elongation at break of the obtained photosensitive polyimide (PSPI) is about 10%. The PSPI has 280°C of Tg and 490°C of 5% weight loss temperature (Sample 1).

To improve the elongation at break, reactive end capping is incorporated to polyimide. 3-Ethynylaniline (EA, Tokyo Kasei) was used as an end capping agent. The PSPI shows 20% of elongation, 280°C of Tg and 482°C of 5% weight loss temperature (Sample 2).

To increase glass transition temperature (Tg) of polyimide, rigid unit is incorporated to dianhydride structure. Pyromellitic dianhydride (PMDA, Daicel Chemical) was used instead of ODPA. The obtained PSPI shows 10% elongation, 330°C of Tg and 492°C of 5% weight loss temperature (Sample 3).

In addition, 5wt% of thermal cross-linker (MX-270, Sanwa Chemical) was added to sample 1 (sample 4). The obtained PSPI exhibits 6% of elongation, 303°C of Tg and 453°C of 5% weight loss temperature.

Long term heat stabilities of those four types of PSPIs were examined. First PSPI using ODPa was examined. The molecular weight of the PSPI sample 1 is about 10K in order to add good photo-lithographic properties. So the physical property such as elongation at break of the sample was not so good. Consequently, elongation of the sample 1 at 200°C after 2000h was poor.

In order to improve physical properties, ethynyl group was incorporated in polyimide end. The ethynyl groups cause the molecular extension during PSPI curing process. So the elongation of sample 2 was 20%. We expected the sample maintained the elongation after 2000h at 200°C. But obtained result was not satisfied.

To improve long term heat stability of PSPI, we designed to use PMDA instead of ODPA in polyimide backbone. PMDA seems to be less reactive than ODPA due to its chemical structure. Polyimide in ODPA unit may decompose as shown in Fig.2 [3]. And PMDA polyimide has higher Tg due to its rigid structure. However the result is not satisfied. Elongation decreased.

Elongation is determined by entanglement of polymer chain. So decrease of elongation during high temperature may occur the chain scissoring and oxidative cross-linking in polymer back-bone. Oxidative cross-linking may occur at phenol unit in polyimide (Fig.3).

To protect the OH group in polyimide back-bone, N-methoxymethyl cross-linking compound (MX-270) added to the PSPI. The MX-270 will react with adjacent position of aromatic OH group as shown in Fig.4 [4].

We expect the MX-270 reaction protects the oxidative cross-link reaction. In addition, MX-270 made the sample elongation high at 15%. Some cross-links in polyimide may increase the
entanglement. Despite the expectation, PSPI sample having MX-270 decreases its physical properties drastically.

![Cross-link reaction of N-methoxy-methyl compound](image)

Fig. 4 Expected Cross-linking reaction of N-methoxy-methyl compound

The cross-link reaction increases the Tg of compound and brittleness. In addition MX-270 does not have heat stable aromatic group, the cross-linked compound may decompose at the MX-270. We assume the MX-270 is not stable at 200°C for long term.

So we thought that the molecular flexibility and chemically stable at 200°C were important to improve long term heat stability. Next we use co-polymerization with some rigid unit in the polyimide back-bone. The obtained PSPI sample shows 10% elongation at break, 506°C at 5% weight loss temperature, and 320°C of Tg. The sample exhibited the no elongation decrease after 200°C for 2000h treatment.

4. Conclusion

In order to improve long term heat stability (such as 200°C for 2000h) of photosensitive polyimide, we examined the polyimide chemical structure, end-capping group, and cross-linker.

ODPA polyimide and PMDA polyimide in this work did not show good long term heat stability. Ethynyl end capping was not effective for improvement of long term heat stability. N-Methoxymethyl cross-linker made PSPI weak for long term heat stability. We obtained stable PSPI by applying some rigid dianhydride in polyimide back-bone. Those results are quite useful for developing good reliable PSPI.

References