Positive-Working Photosensitive Polyimide Based on Crosslinking and Decrosslinking Reaction of Vinyl Ether Crosslinker

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ABSTRACT

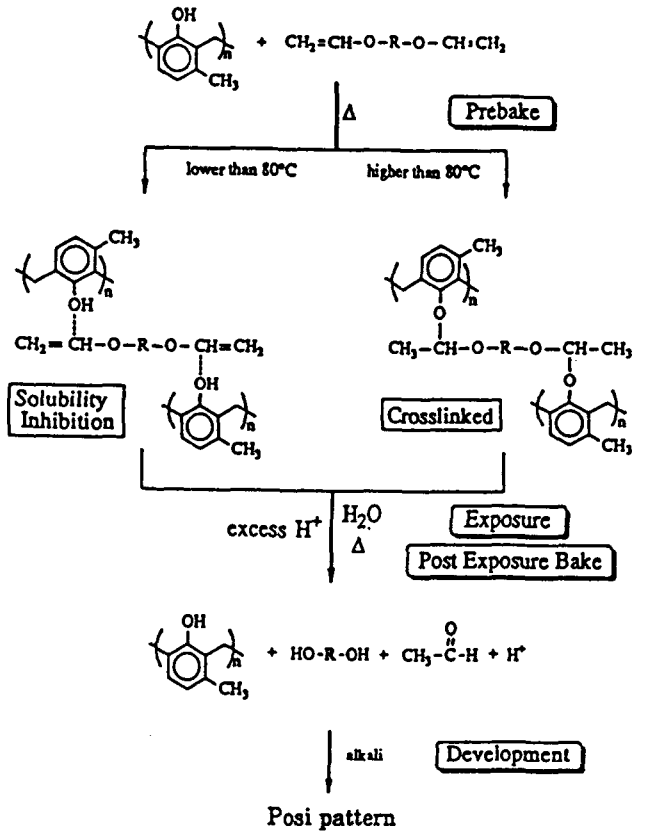
Positive working photosensitive polyimides and the derivatives based on the reaction of vinyl ether and acidic site in polyamide acid were designed and synthesized. The photosensitive polyimides consist of polyimide precursor with acidic group, vinyl ether crosslinker and photoacid generator. Positive-working photosensitive polyimides and the derivatives were synthesized by utilizing the specific reactions occurring between vinyl-ether group and poly(amide-acid). Composition of the photosensitive polyamide is composed of NMP solution including poly(amide-acid), bi-functional vinyl- ether monomer and a photoacid generator. A Si-wafer was coated with the solution and was dried at 120C for 3 minute in a oven. The photosensitive layer on the Si-wafer was exposed to 365nm light and then developed in an aqueous base. The pattern that was formed on the wafer consists of the crosslinked poly (amide-acid) and a small amount of unreacted vinyl ether monomers. Successively, poly(amide-acid) forming the pattern was converted to poly(imide) by baking at 250C for 2 minute. The advantages and characteristics of photosensitive polyimide synthesized by novel mechanism will be described.

INTRODUCTION

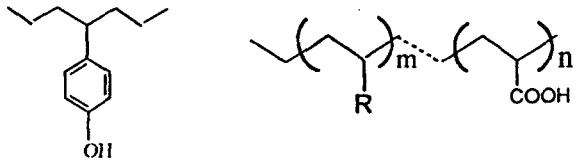
Polymers having protic groups in their structure are crosslinked by multifunctional vinyl-ether to form acetal bonds. The acetal bonds are known to be very sensitive to acid, and are dissociated in the presence of acidic compounds. The reaction of vinyl-ether group provides a new mechanism to design the positive- working photoresists. Some photoresists with the high resolution have been developed based on the reaction of bifunctional vinyl-ether compound and phenol-novolak resin.

This photoresist consists of essentially 3 kinds of components, which are a polymer containing phenol groups in themselves, bifunctional vinyl-ether monomer that plays a role of crosslinker, and a photoacid precursor that generates acid by UV exposure. The reaction path occurring between vinyl-ether and phenol groups is exhibited by the flow-chart below. Figure 1 shows mechanism where the reaction mentioned here offers the positive-working photoresist.

The reaction occurring between phenol groups existing in the polymer and vinyl-ether compound is explained by flow-chart below. Figure 1 shows mechanism where the reaction mentioned here offers the positive-working photoresist.

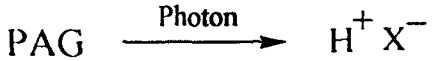


Examples of Polymer with Acidic Groups

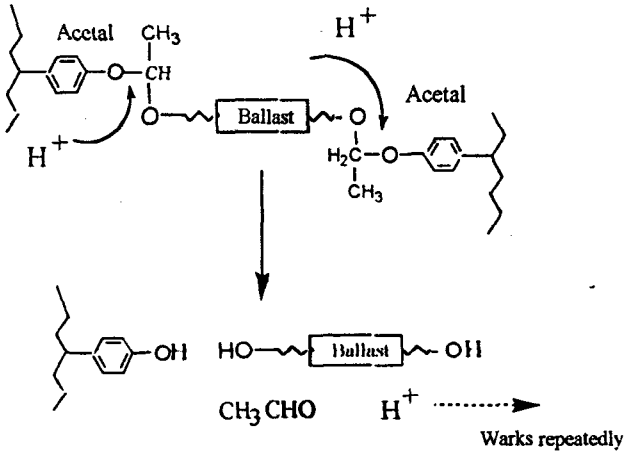


Vinyl Ether crosslinker

Photoacid Generator



Reaction Model of Crosslinking and Decrosslinking

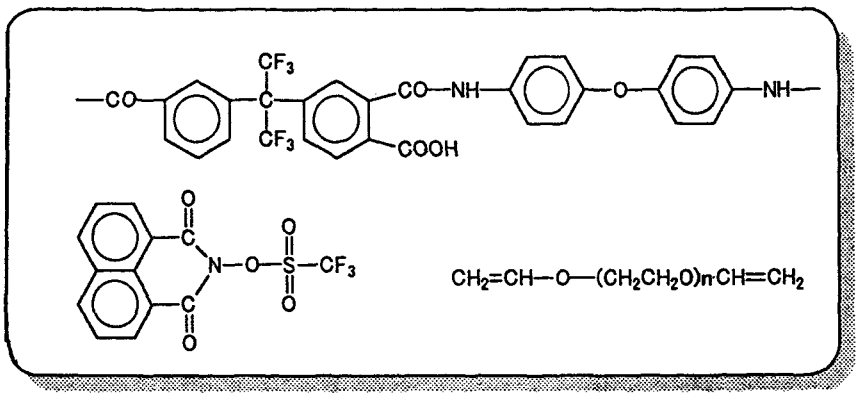


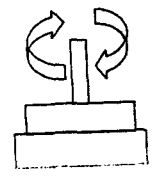
Application of Vinyl Ether to Photosensitive Polyimide.

Several photosensitive polyimides offering positive tone behavior have been reported so far. Mechanism of their positive tone behavior are based on mainly three principles, mixing NQD to polyamide acid, elimination of blocking agent of acid groups existing in polymer itself in order to prompt the cyclization of polyamide acid.

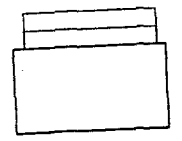
In the present research, we propose a novel reaction mechanism to design the positive working. Vinyl ethers react with acidic groups such as carboxyl, sulfonyl and hydroxyl groups to form acetal band. It is well known that acetal groups are very sensitive to protic hydroxyl group and dissociated easily in the presence of acid. The reactions between vinyl ether group and protic hydroxyl group were applied to design the photnsensitive polyimide. The photosensitive polyimide proposed here is composed of reaction occurring between vinyl ether and protic hydroxyl groups in polymer.

The typical composition of the photosensitive polyimide consists of three components, poiyamide acid or soluble polyimide, bifunctional vinyl ether monomer and photoacid generating compound. The flow chart indicating an outline of reaction path of the photosensitive polyamid acid and the patterning process are illustrated below. According to the reactions mentioned here, any polyimides as well as the precursors containing acidic group in their structures are converted to photosensitive polyimide by adding vinyl ether crosslinker and PAG. Among these components, polymers decide the thermal stability, vinyl ether crosslinkers govern the patterning property of photosensitive polyimide such as high sensitivity, low swelling property and high resolution. Photoacid generators are a gate to photon energy and decide the wavelength of exposing light, and efficiency for dissociation of acetal bonds. The patterning process is as follows; The NMP solution containing polyamide acid, bifunctionnl vinyl ether, and photoacid generator were spin-coated on a Si-wafer and dried at 110 C. for 2 min to form photosensitive layer with about IO micron meter thickness. The layer was exposed to 365nm light, using an ultrahigh pressure mercury lamp for various time followed by post-exposure bake for 60sec at 180C. The exposed layer was developed with an aqueous base, 2. 38% TMAH. The developed layer was dried, and cured in nitrogen atmosphere for 1 hour at 100-350 C. then observed by a microscope. An example of patterned poly(amide acid) is shown in pictures and those pictures demonstrate that 3-5 micron meter line & space patterns are clearly resolved. Sensitivity curves, development characteristics and patterns size reproduction are shown in Figure 3. 4, and 5. Figure 3 indicates the sensitivity for this photosensitive

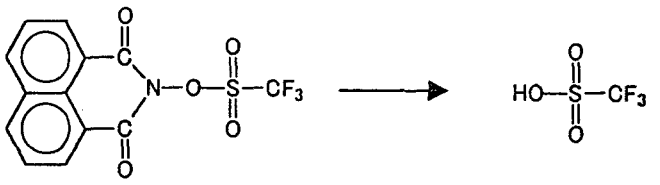


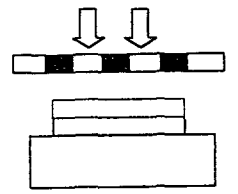


Spin-coating on a silicon wafer

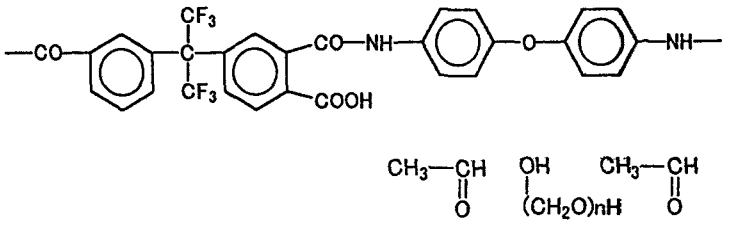


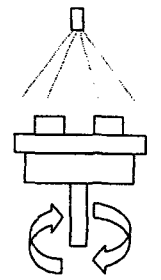
Prebake





Imagewise exposure





Development

Fig.2 Patterning process of photosensitive polyimide proposed in the present research.

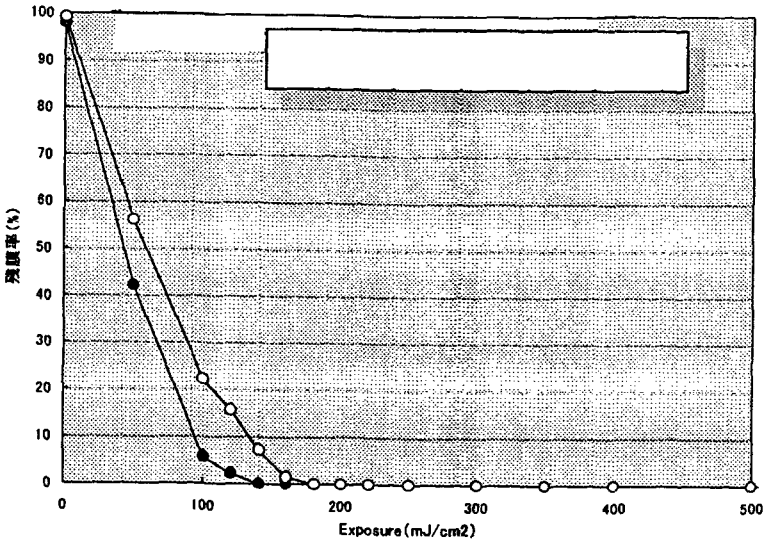


Fig.3 Sensitivity curves of photosensitive poly(amide acid)

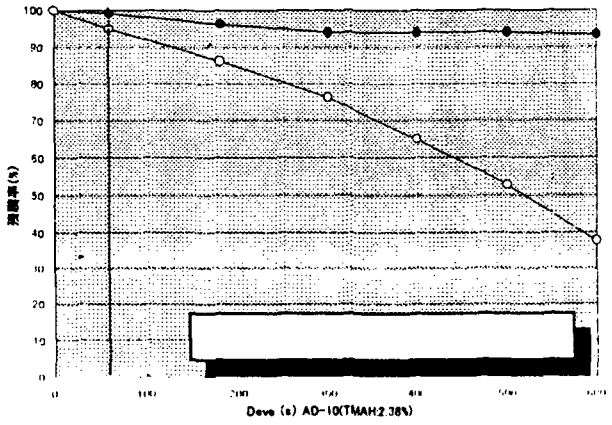


Fig.4 Remained Film as a function of developing time(s)

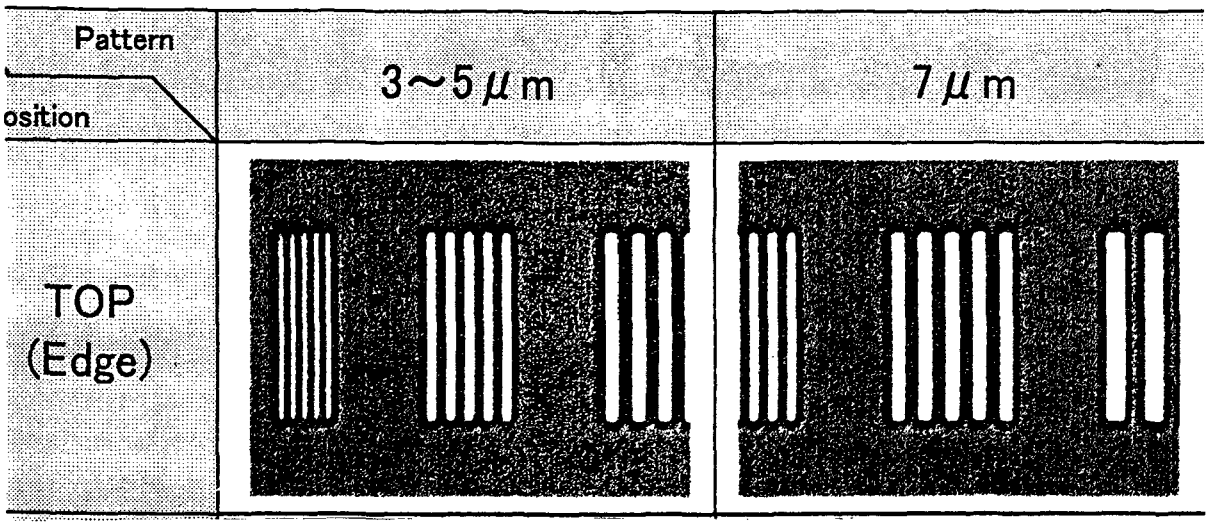


Fig.5 Pictures of polyimide patterns (Film thickness: 10 micron and resolution : 3 – 5, and 7 micron L&S)

polyimide is 150 mJ/cm2, and this sensitivity value for 10 micron meter thickness is considered as high sensitivity compared with other photosensitive polyimide reported so far.

Another polyimide precursor has structure shown below. In this precursor, carboxyl groups are esterified with p-hydroxyl benzyl alcohol where the acidity of aromatic hydroxyl group is lower than that of carboxyl group. Similar characteristics to those for ploy (amide acid) were observed. The resolution of line & space is improved while the sensitivity value was a little lower.

In addition to polyimide reported here, some other photosensitive polyimides have been synthesized where polymers. crosslinkers and photoacid generators were varied. More details will be reported in Conference.