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Studies of the chemically amplified development-free vapor photolithography

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Abstract

Development-free vapor photolithography (DFVP) is a unique all-dry pattern transfer technique, which is based on the reaction of SiO_2 with HF vapor under a polymer film in the presence of accelerators at a temperature of above 100°C. In this paper, we found that the etching reaction could be catalyzed by superacids. Based on this discovery, a novel, chemically amplified, development-free vapor photolithography technique was developed, and has been successfully applied to power electronic device manufacture. © 1997 Elsevier Science S.A.

Keywords: Development-free vapour photolithography; Chemical amplification; Diphenyliodonium salts; Photosensitizer

1. Introduction

Development-free vapor photolithography (DFVP) is a unique all-dry pattern transfer technique and has been successfully used in manufacturing microelectronic devices. The general procedure of development-free vapor photolithography is illustrated in Fig. 1. A silicon wafer is coated with cinnamate-type photopolymer containing 5-nitroacenaphthene as a photosensitizer, followed by masking and exposure to UV light. Then an etching gas (hydrofluoric acid vapor) is passed over the wafer in a chamber at a temperature of above 100°C for a definite time (shown in Fig. 2). The SiO_2 under the polymer film in the exposed area is etched and removed completely. However, the SiO_2 in the unexposed area remains and forms a clear positive pattern. This process eliminates the need for development and post-baking in the conventional wet photolithography process. In spite of exposure to UV light, a high-resolution pattern can be obtained (with as low as 0.4 μm etching lines). Moreover, the DFVP process also overcomes the problem of isotropic etching and results in a high aspect ratio (12:1) [7]. The question why a polymer film that resists etching in conventional wet photolithography becomes an etch-inducing film in DFVP has attracted the attention of many researchers [1–9].

A mechanism (shown in Scheme 1) has been proposed. During the DFVP process the reaction of SiO_2 with HF vapor can only occur when etching accelerators exist. These accelerators are compounds containing polar functional groups that can absorb and ionize HF vapor at high temperature. After exposure to UV light, the photopolymer is cross-linked and its T_g is increased. This prevents the rapid escape of small molecular accelerators contained in the film, such as 5-nitroacenaphthene which has been confirmed to be an effective accelerator. Consequently, there is a difference of accelerator concentration between exposed and unexposed areas. In the exposed areas the HF vapor can etch SiO_2 with a measurable rate in the presence of accelerators. In the unexposed areas the etching reaction cannot occur because the accelerators escaped from the film at high temperature. A recent research demonstrates that polymers with carbonyl, nitro, amino for-

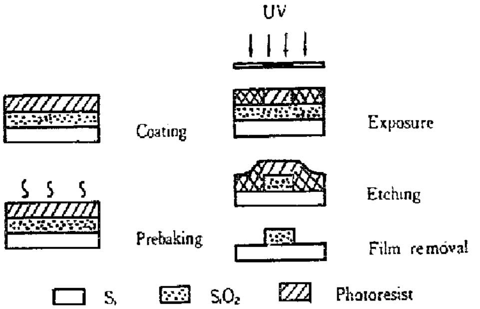

Fig. 1. Schematic illustration of the DFVP.

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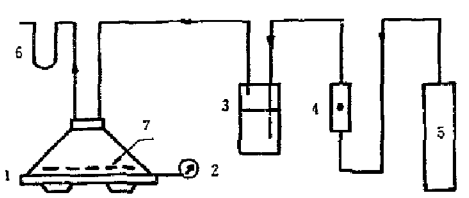


Fig. 2. Schematic illustration of the etching system. 1, hot plate; 2, temperature controller; 3, hydrofluoric acid; 4, flowmeter; 5, nitrogen source; 6, pressure meter; 7, silicon wafer.

$$SiO_2(s) + HF(g) \overset{>100°C}{\not\longrightarrow} SiF_4(g) + H_2O(g)$$

$$SiO_2(s) + HF(g) \xrightarrow[>100°C]{Accelerator} SiF_4(g) + H_2O(g)$$

$$Accelerator + HF(g) \longrightarrow [HAccelerator]^+ + F$$

Scheme 1.

macyl, and other polar functional groups can also act as accelerators of the etching reaction of SiO_2 with HF [8].

It is well known that the T_g of the polymer is affected by crosslinking density. However, only high crosslinking density can markedly increase T_g, so in DFVP a high exposure dose is needed. The use of DFVP for making 0.7 μm features has been reported at a relatively high exposure dose (e.g. 1.5 mJ cm^{-2} for UV; 3.2 mC cm^{-2} for 20 keV e-beam) [3]. In addition, even in the exposed area the small molecular accelerators may gradually escape from the polymer film at an etching temperature above 120°C. Therefore, the etched thickness of SiO_2 is limited (less than 1.0 μm). These drawbacks prevent the application of DFVP.

At present, we find that this etching reaction could be catalyzed by the superacids. When simple diphenyliodonium salts or triphenylsulfonium salts are used as photosensitive acid generators, in the exposed areas, the HF vapor can etch SiO_2 with a measurable rate in the presence of the superacids. However, in the unexposed areas the etching reaction cannot occur because of the absence of the superacids. Because only catalyst doses of superacids are required, the exposure energy can be reduced to 600 mJ cm^{-2}, even if 365 nm UV serves as an irradiation source, and the etched thickness of SiO_2 can attain to 1.6 μm.

Although most triarylsulfonium and diaryliodonium salts absorb strongly at wavelengths near 250 nm, their absorption at longer wavelengths is comparatively low. The poor absorptivity of these photoinitiators in the 300–450 nm region is of particular concern since it severely limits their efficiency or light utilization in the region in which the commonly available high pressure mercury lamps provide substantial portion of their emission. However, a photosensitizer can be used to extend the wavelength of these oniums into the near-UV region. We found that diaryliodonium salts can be reduced by easily oxidizable radicals generated from typical free radical photoinitiators, such as Ciba 184 (hydroxy-cyclohexyl phenyl ketone). The mechanism is as proposed in Scheme 2 [10]

2. Experimental

2.1. Equipment

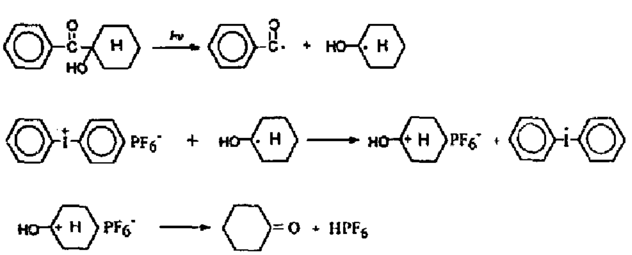
Conventional spin-coating and exposure units were used. The etching system consisted of a vapor etching chamber with a hot plate, attached to a temperature controller and a vapor source. The vapor was a mixture of water, HF, and N_2 supplied from a bubbler containing 40% hydrofluoric acid solution with a N_2 feeder at room temperature (Fig. 2).

2.2. General procedure

(1) Spin coating at a speed of 3000 rpm, the film thickness was 500–600 nm. (2) Prebaking: 15 min at 70–80°C. (3) Exposure: high pressure mercury light 125 W; ultraviolet lights with wavelengths greater than 300 nm were used and the light intensity was 10–12 mW cm^{-2}; exposure time 45–60 s. The resolution photomask was used. (4) Etching: the etching temperature was adjusted by a temperature controller; N_2 flow: 0.25 l min^{-1}; gas pressure, 2.6 Pa. The etching rate was determined by the etched thickness of SiO_2 measured by color comparimetry within a definite time.

2.3. Materials

5-nitroacenaphthene, poly(glycol cinnamalmalonate), Ciba 184 (1-hydroxy cyclohexyl phenyl ketone, benzoic acid, p-toluenesulfonic acid and ethylene glycol monoethyl ether are commercially available. Diphenyliodonium salts



Scheme 2.

with complex metal halide anions such as PF_6^- were prepared according to Crivello and Lam [11]. All the materials were purified before use. Silicon wafers with SiO_2 surfaces were obtained from the power electronic devices factory of Tsinghua University, and the thickness of SiO_2 is over 1500 nm.

2.4. *Resist of DFVP preparation*

This chemically amplified DFVP system was formulated by dissolving 10 wt.% poly(glycol cinnamalmalonate), 0.3 wt.% 5-nitroacenaphthene, 0.5 wt.% Ciba 184 and 0.2–1.0 wt.% diphenyliodonium salts in the solvent, 2-ethoxyethyl acetate.

3. Results and discussion

3.1. *Effects of exposure on the etching reaction*

As can seen from Figs. 3 and 4, with the increase of exposure energy the etching reaction rate increased because of the increase in the concentration of the generated superacids, and the etched thickness of SiO_2 attained to 1.6 μm. However, The required exposure energy is still too high. A cinnamate-type photopolymer was used in this research, which plays a role of a film former. However, this polymer film has a strong absorptive peak centered at 328 nm [9], so it can compete with Ciba 184 to absorb the UV. This will result in the decrease of the photosensitivity. Therefore, when this polymer film is substituted by transparent photopolymers, a DFVP system highly sensitive to near-UV exposure will be obtained due to chemical amplification.

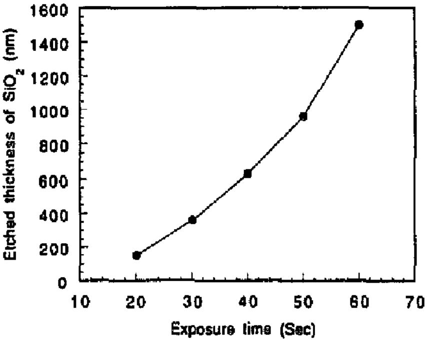


Fig. 3. The plot of etched thickness of SiO_2 vs. exposure time, etched at 120°C for 30 min (8.5 wt.% diphenyliodonium salts in the polymer film).

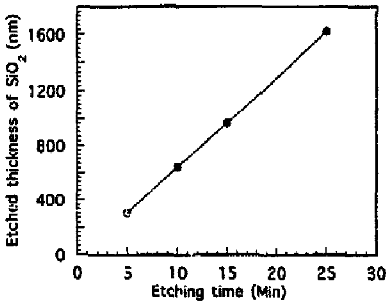


Fig. 4. The plot of etched thickness of SiO_2 vs. etching time (8.5 wt.% diphenyliodonium salts in the polymer film).

3.2. *Effects of the strength of acid catalysts on the etching reaction*

As can be seen from Fig. 5 and Table 1, the superacids play a central role in the etching process of DFVP. Fig. 5 shows that the etching rate strongly depends on the concentration of diphenyiiodonium salts and Table 1 proposes that the strength of acid is also very important. Benzoic acid is a kind of weak acid, and it cannot promote the reaction of SiO_2 with HF. Although p-toluenesulfonic acid (stronger than HNO_3) can catalyze the etching reaction, however, compared with superacids (such as HPF_6), it is not satisfied.

This acid-catalyzed etching reaction was initiated by the attack of radiochemically generated superacids onto the backbone oxygen atoms of SiO_2, as illustrated in Scheme 3. As a result, the bond which links oxygen with silicon was weak-

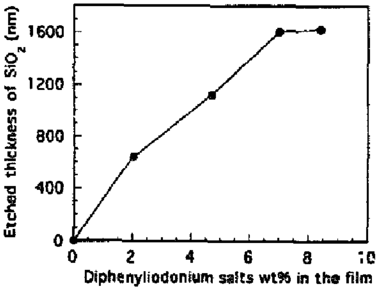
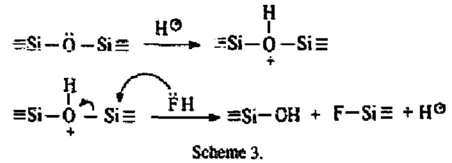


Fig. 5. The plot of etched thickness of SiO_2 vs. weight percentage of diphenyliodonium salts, etched at 120°C for 25 min.

Table 1
Effects of the strength of acids on the etching reaction

Acid	Weight percentage	Etching time (min)	Etched thickness of SiO_2 (nm)
HPF_6	catalyst dose	25	> 1600
p-Toluene-sulfonic acid	7.5	30	1000
Benzoic acid	7.3	30	0



Scheme 3.

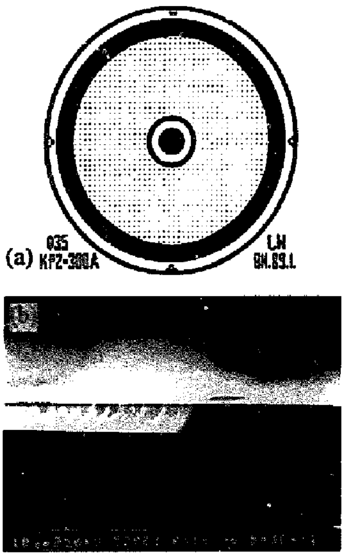


Fig. 6. The cathodic pattern of the KP300A power thyristor. (a) Overall picture obtained by photography. The cathode emitter shorts are 160 μm in diamater, and the distance between two adjacent shorts is 700 μm. The center gate has a diameter of 3.8 mm. (b) The etched SiO_2 layer pattern obtained by SEM.

ened and then HF attacked the backbone silicon atoms of SiO_2.

4. Summary

At a temperature of above 100°C, superacids (such as HPF_6) can catalyze the reaction of SiO_2 with HF. The etching rate was affected not only by the concentration of the acids, but also by the strength of the acids. A difference of superacid concentration between exposed and unexposed areas can be made through the photolysis of diphenyliodonium salts. Based on these research results, a novel, chemically amplified, development-free vapor photolithography technique was developed, and has been successfully applied to the power electronic device manufacture. Fig. 6 shows the cathodic pattern of the KP300A power thyristor, which is obtained by the DFVP process. As can be seen from Fig. 6(b), when the thickness of SiO_2 is less than 700 nm the wall is nearly vertical. However, with the increase of the thickness of SiO_2, the wall became sloping. We think this is because the film is difficult to fall down during the etching period.

Acknowledgements

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