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# SELECTIVE DEPOSITION OF SILICON OXIDE AND IT'S APPLICATION

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Selective deposition technology of thin film has advantages for planarization, self alignment and the fine lithography process for integrated circuit fabrication. Selective deposition of $SiO_2$ film has been reported by only a few investigators[1,2], in spite of it's potentiality of wide application. In this report, a new type of selective deposition of silicon oxide using the surface energy difference between materials, and it's application for fine lithography, are proposed. Poly-perfluoro alkyl acrylate (PPFAA) is used as a selective deposition mask. The PPFAA has perfluoro alkyl side chains which significantly reduce surface energy and are expected to prevent film formation. It also behaves as a nega type resist by an electron beam. A gaseous mixture of $SiCl_4$ and $H_2O$ is used as the deposition gas.

The experimental reactor of selective deposition is shown in Fig. 1. The total pressure of this reaction system is atmospheric pressure. $SiCl_4$ and $H_2O$ gases introduced into the reactor from a ring pipe with the $N_2$ carrier gas. Under the condition that thin film is formed on Si, $SiO_2$ and OFPR resist, no deposition reaction occurs on PPFAA. The deposition rate on Si and the nuclei occupied area ratio to total PPFAA area are plotted as a function of the gas flow rate in Fig.2, and nucleation on PPFAA by SEM observation is shown in Fig.3. Deposition selectivity increases with decreasing reactive gas flow rate as shown in Fig.2, Fig.3.. Under a low reactive gas flow condition, nuclei formation on PPFAA can be suppressed. This phenomenon can be explained as follows. Nuclei formation on PPFAA is likely to be analogous to stable cluster formation in super saturated vapor. The activation energy of stable cluster formation can be written as $G \propto A/k^2T^2(\ln P/P_0)^2$ where P and $P_0$ are vapor pressure and saturated vapor pressure, respectively, and A is dependent on surface material. So the difference of nucleation energy between that on PPFAA film and that on other materials increases with decreasing gas pressure.

The infrared absorption spectra of the deposited film is shown in Fig.4. In addition to well known $SiO_2$ bands, SiOH and $H_2O$ bands are contained. These spectra indicate the following. Surface reaction between $SiCl_4$ and $H_2O$ produces HCl and silicon oxide containing the OH radical. SiOH and $H_2O$ on the deposited silicon oxide surface behave as self-catalysts for deposition reaction.

This technique can be applicable to form fine mask patterns for etching and implantation. The schematic process flow of the application to fine pattern formation is shown in Fig.5. Thin PPFAA film is coated on resist film. The PPFAA film is irradiated by an electron beam (Fig.5-a). The unexposed PPFAA can be selectively dissolved away by $CCl_2FCClF_2$ (Fig.5-b). Next, the sample is treated with gaseous $SiCl_4$ and $H_2O$ at room temperature. The silicon oxide film is selectively formed on the resist area (Fig.5-c). The resist pattern is formed by RIE.(Fig.5-d).

A SEM photograph of an application example to a dry etching mask is shown in Fig.6. Resist patterns with 0.12μm line and 0.08μm space were obtained by reactive ion etching with a selectively deposited silicon oxide mask.

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REFERENCES
(1) Smith, Thin film Solid Films vol,96, 161, 1982
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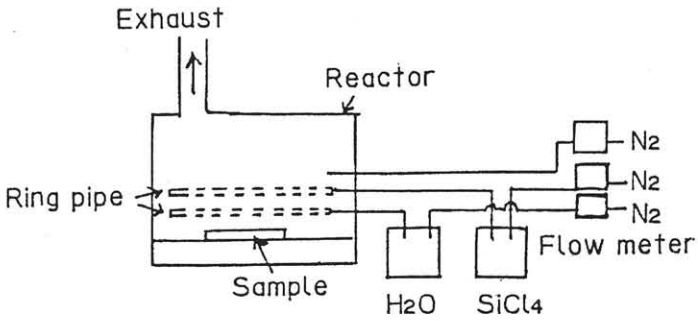



Fig.1 Experimental reactor

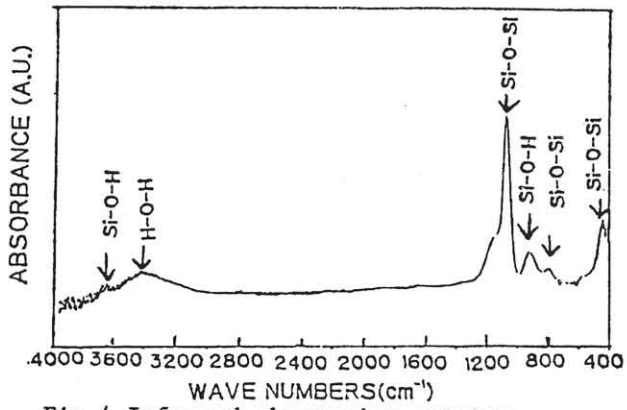



Fig.4 Infrared absorption spectra

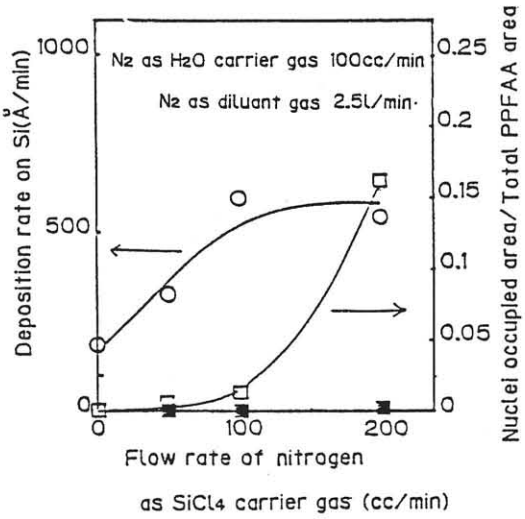



Fig.2 Flow rate dependence of deposition rate and nuclei formation
Deposition rate on Si(left side):(O)
Nuclei occupied area/Total PPFAA area (right side)
when 1000Å thick film deposited on Si: (■)
when 2000Å thick film deposited on Si: (□)

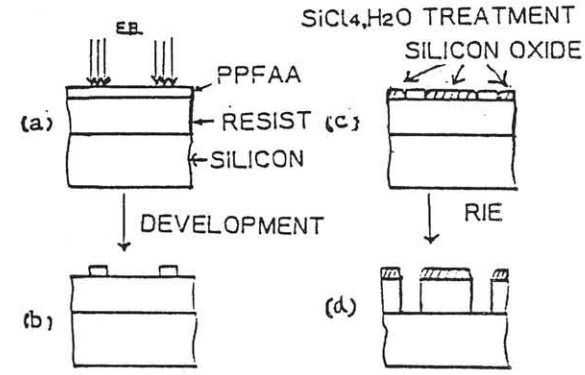
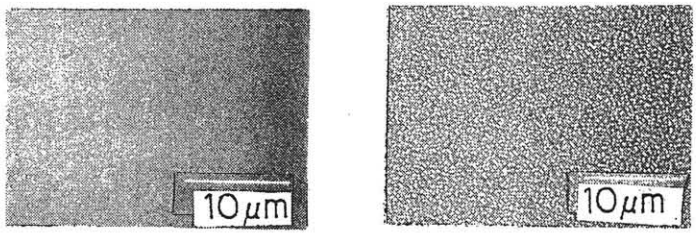
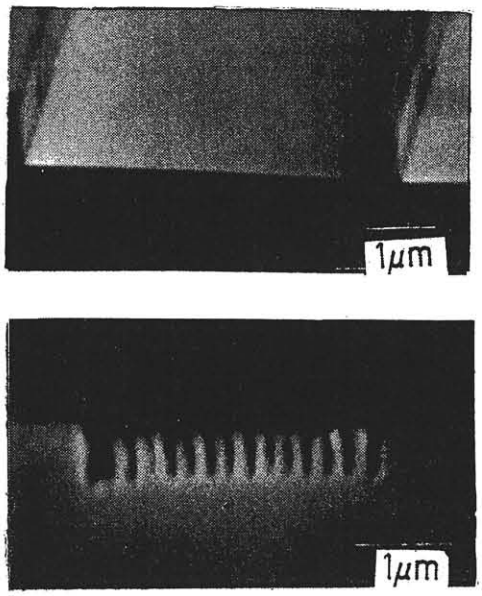



Fig.5 Process flow of the application to fine pattern formation




(a) (b)

Fig.3 SEM photograph of PPFAA surface when 2000 Å thick film deposited on Si at the flow rate of $N_2$ as $SiCl_4$ carrier gas
0cc/min (a)
200cc/min (b)




(a)
(b)

FIG.6 SEM photograph of
0.2μm isolated pattern (a)
0.12μm line and 0.08μm space (b)