
SHORT COMMUNICATIONS

Stain Film Formed Photochemically on Silicon

By Yasuo NAKAI

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It is known that stain film can contribute to the stabilization of transistors.¹⁾ The stain film has been obtained hitherto by reaction with hydrogen fluoride-nitric acid²⁾ or by anodic oxidation in hydrogen fluoride solution.³⁾

In this experiment, it was found that the formation of stain film can be effected by the photochemical reaction of HF-O_3 with silicon crystal. For example, oxygen gas (1200 cc./min.) containing 5% ozone (in weight) and HF-N_2 gas (500 cc./min.) was brought into

contact with the (111) surface of 2- to 80-cm-cm. n-type silicon crystals for 0.5 to 2 hr. at room temperature and under irradiation from a high-pressure mercury lamp (1 kW.) through filters transmitting at 5800, 5460, 4358, 4047 and 3650 Å. Ozone was obtained by a silent discharge. The mixture of HF-N_2 gas was obtained by bubbling nitrogen gas through a 24N hydrogen fluoride solution at 25°C.

It was found to be necessary, for the formation of stain film, to irradiate the silicon surface with photons of energy higher than approximately 2.7 eV.

Infrared, optical absorption, electron spin resonance and solid mass spectra were investigated in studying the physicochemical properties of stain film.

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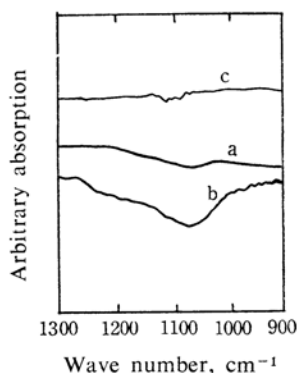


Fig. 1. The infrared spectra of stain film (a) before and (b) after thermal treatment at 250°C for 10 hr., and (c) of silicon crystal.

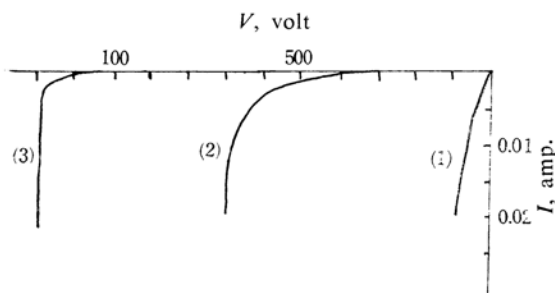


Fig. 2. Reverse characteristic (I - V curve) of a p^+-n diode on which stain film was photochemically formed.

(1) Before heat treatment (2) after being kept at 250°C for 2 hr. in air, and (3) after being kept at 250°C for 10 hr. in air.

Figure 1 shows the infrared spectrum of stain film. The band at 1080 cm^{-1} , whose intensity is weak before heat treatment (as is shown by curve 1a), appears strongly after being kept at 250°C for approximately 10 hr. in air (curve 1b). The band at 1080 cm^{-1} is assigned to the Si-O stretching mode; its shape is similar to that of amorphous silica.

The electron-spin resonance-absorption curve of stain film at an operation microwave frequency in the vicinity of 9.2 kMc./sec. exhibits three peaks ($g_1=2.0068$, $g_2=2.0048$ and $g_3=2.0000$) at 77°K. Two optical absorption bands were observed, at 7500 Å and 5000 Å. Silicon, oxygen and fluorine atoms were detected in stain film by solid mass spectroscopy, but its molecular formula is not clear at present.

Stain film was photochemically formed upon the junction of mesa p^+-n diodes. A typical variation of the reverse I - V curve with aging is shown in Fig. 2. Diodes had a very inferior reverse characteristic just after forming stain film, but the breakdown voltage became stable and the drift decreased after they had been kept at 250°C for 10 hr. in air.⁴⁾

Central Research Laboratory
Tokyo Shibaura Electric Co., Ltd.
Kawasaki-shi, Kanagawa

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