Properties of Fluorinated Polyimide Films Prepared by Vapor Deposition for Multilevel Interconnection

層間絶縁膜用フッ素化ポリイミドの特性

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Abstract

The polyimide films were prepared by vapor deposition polymerization (VDP). A fluorinated diamine and a fluorinated dianhydride monomer were evaporated individually, and polymerized on a Si substrate. Fluorinated polyimide (FPI-2) which includes 23 % fluorine, and FPI-6 which includes 43% fluorine, have the low dielectric constant (FPI-2:ε = 2.55, FPI-6:ε = 2.95) and the thermal stability above 400°C (FPI-2), above 500°C (FPI-6). Both polyimides exhibit a steady electrical character. Secondary ion mass spectroscopy showed that the polyimide film prevents thermal diffusion of Cu at 400°C (FPI-2), 500°C (FPI-6). Etching of the polyimide films with SiO_2 mask was performed without over-etch using O_2 plasma. Cu deposition on the etched polyimide films and chemical mechanical polishing were also examined. As a next generation material, we are developing low density (porous) polyimide films.

Introduction

Interlayer dielectrics (ILDs) of ULSI multilevel interconnections require low dielectric constant because of many problems in circuit performance, such as power dissipation, crosstalk and signal propagation delay. Organic materials are known to exhibit significantly lower dielectric constant than inorganic oxides, so that many researchers studied organic ILDs.

Fabrication of organic ILDs will help advance the study of organic ILDs towards next stage.

The application of parylene-N and amorphous-fluorinated carbon, which can be prepared with dry process, have been reported as ILDs application. These materials exhibit a low dielectric constant. But a major problem is that these materials do not have enough thermal stability. The presence of large substituted groups or fluoro groups in the molecular skeleton increases the free volume and reduces polarization [1]. The dielectric constant is therefore lowered. Furthermore, thermal stability of polyimide can be raised with rod-like structure [2]. This paper investigates the use of fluorinated polyimide films as interlayer dielectrics of ULSI multilevel interconnections.

Experimental

The fluorinated polyimide films were prepared by vapor deposition polymerization from a fluorinated diamine and a fluorinated dianhydride on a Si substrate. Imidization was performed in furnace under N_2 gas at 400°C for 1 hour. The thermal stability of the fluorinated polyimide was evaluated with Thermo-Gravimetric Analysis or by measuring decomposition gas pressure. Cu diffusion into the fluorinated polyimide film was detected by secondary ion mass spectroscopy. The dielectric constant was calculated from the measurement of the fluorinated polyimide capacitance with impedance analyzer and the film thickness.

Result and Discussion

Fig. 1 shows the relationship between fluorine content and the dielectric constant of fluorinated polyimide (FPI-2) which includes 23 % fluorine, and FPI-6 which includes 43% fluorine, have the low dielectric constant (FPI-2:ε = 2.55, FPI-6:ε = 2.95), respectively. Outgassing from those polyimides caused by thermal decomposition is shown in Fig. 2. They were stable above 400°C (FPI-2), above 500°C (FPI-6). Fig. 3 shows relationship between leakage current and applied field at 25°C for FPI-6. The leakage current barely changes up to 1MV/cm [3]. Secondary ion mass spectroscopy shows the polyimide film prevents thermal diffusion of Cu at 400°C (FPI-2), 500°C (FPI-6). Fig. 4 is the depth profiles of FPI-6 before and after annealing. Fig. 5 and Fig. 6 show SEM images for etched FPI-6 film with SiO_2 mask performed by O_2 plasma, for Cu film on the etched polyimide film prepared by sputtering. The planarized film produced by chemical mechanical polishing is shown in Fig. 7. We are developing low density (porous) polyimide films for a next generation material. Fig. 8 shows the low density polyimide film prepared by the vapor deposition method.

Conclusions

The polyimide films were prepared by vapor deposition polymerization. Fluorinated polyimide have the low dielectric constant (FPI-2:ε = 2.55, FPI-6:ε = 2.95) and the thermal stability above 400°C (FPI-2), above 500°C (FPI-6). The leakage current barely increases up to 1MV/cm. Secondary ion mass spectroscopy shows the polyimide film prevents thermal diffusion of Cu at 400°C (FPI-2), 500°C (FPI-6). Etching for polyimide films with SiO_2 mask was performed without over-etch using O_2 plasma. Cu deposition on the etched polyimide films and chemical mechanical polishing were also examined. As a next generation material, low density (porous) polyimide film was developed.

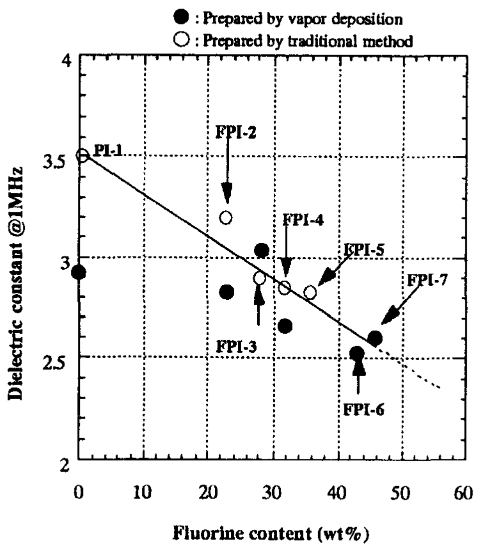

Fig.1 Relationship between constant and fluorine content at in each fluorinated polyimide.

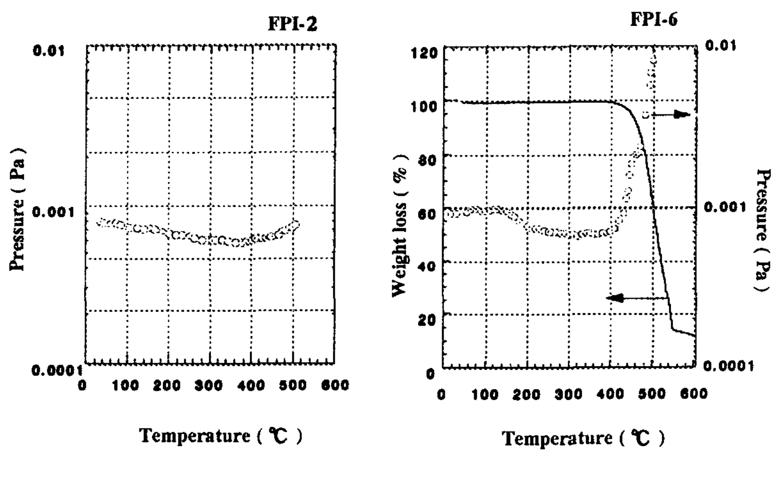

Fig.2 TG and changes in the pressure during the heating of FPI-2 and FPI-6 in a vacuum.

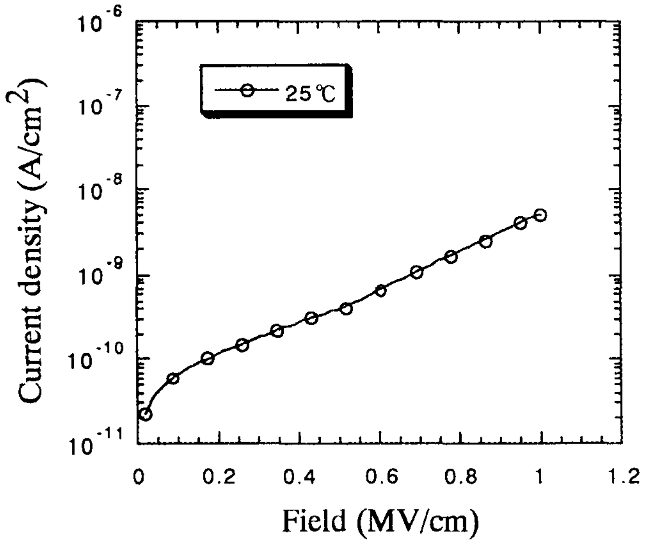

Fig.3 Relationship between leakage current and applied field at 25°C.

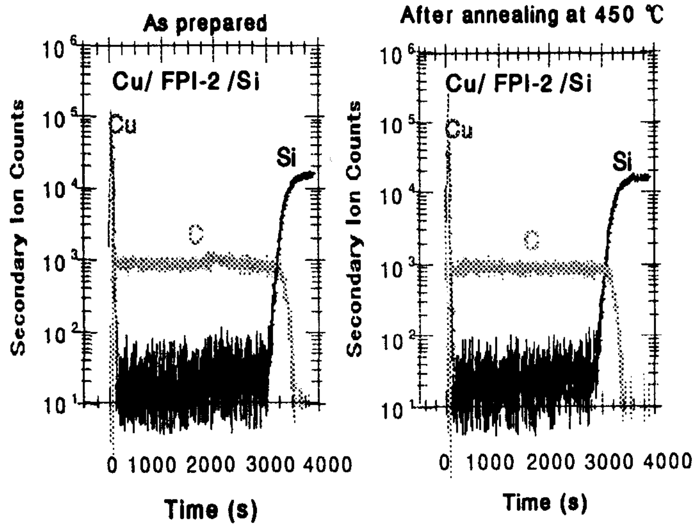

Fig.4 SIMS depth profiles of Cu/FPI-6 before and after annealing at 450°C.

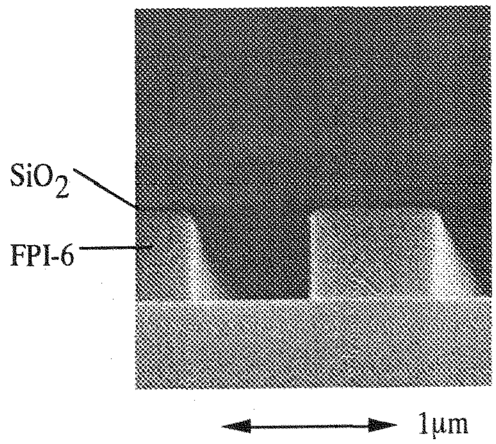

Fig.5 Cross sectional SEM image for the etched FPI-6 film.

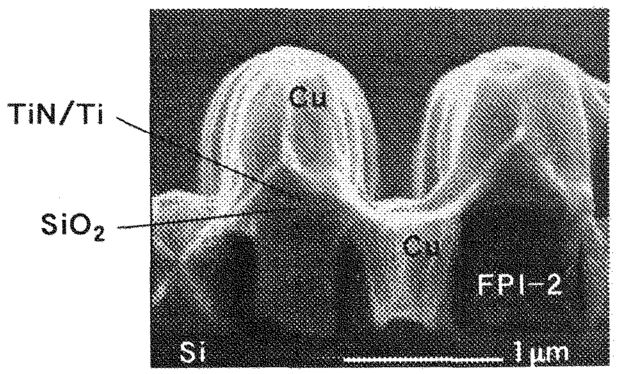

Fig.6 Cross sectional SEM image for gap filling of Cu prepared by sputtering.

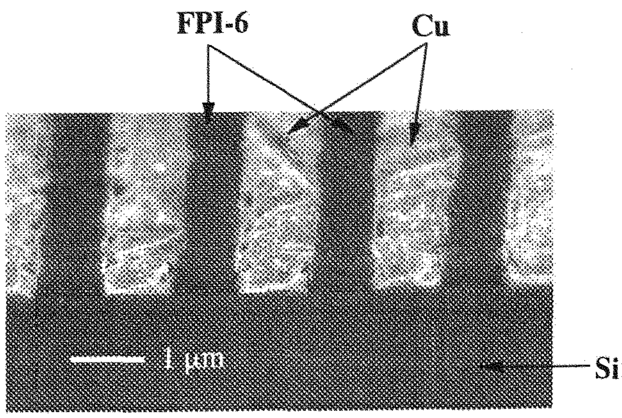

Fig.7 Cross sectional SEM image for the film planarized by chemical mechanical polishing.

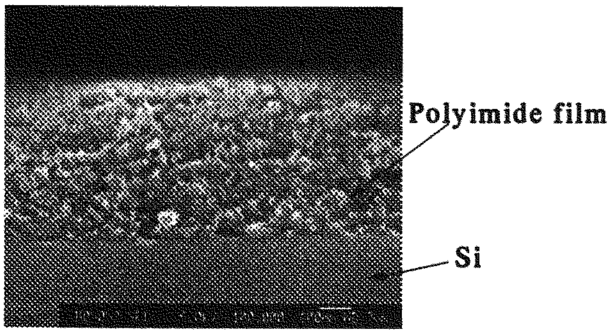

Fig.8 Cross sectional SEM image for the porous polyimide film prepared by the

Reference

1. T.Matsuura, S.Ando, S.Sasaki, and F.Yamamoto, Macromolecules, **27** (22), (1994) 6665.
2. S.Ukishima, M.Iijima, M.Sato, Y.Takahashi, and E. Fukada, Thin Solid Films, **308-309**, (1997) 475.
3. T.-M. Lu, P.S. Ho, S.P. Murarka, and R.J. Gutmann, Proceedings Fourth International DUMIC, (1998) 17-24.