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The Thermal Degradation Prevention of Fluorocarbon Material for Interlayer Dielectric Film

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Recently, the fluorocarbon material that is the candidate for interlayer dielectric film due to an excellent property of low-k is attractive. It is known that the interlayer dielectric film containing F (fluorine) cause degradation of a device performance by high temperature process such as CVD (chemical vapor deposition) and sintering in a back end of line. It has been reported that this degradation is caused by released gases of F from interlayer dielectric film [1]. Therefore, in high temperature process, to prevent F gas release from interlayer dielectric film is very important. The cause of the generation of released gas is as follows. 1) The catalytic effect of metal (barrier metal such as TaN for copper interconnection) surface in contact with the interlayer dielectric film. 2) The oxidization degradation by oxygen or moisture that the interlayer dielectric film contains. We clarified that the best metal material having a low catalytic effect to fluorocarbon material. So far, the systematic and accurate research for the degradation behavior was very difficult because the ultra clean environment could not be created. And now, we have developed the ultra-high purity gas supply technology. It means we have obtained the ultra clean environment using this technology. In this paper, we report the thermal degradation behavior for fluorocarbon resins (This fluorocarbon resin is the imitation material of fluorocarbon material for interlayer dielectric film) under ultra clean environment. We clarified that the best metal material having a low catalytic effect to fluorocarbon material. Fig.1 shows a schematic diagram of experimental setup to analyze the released gases from sample by thermal degradation. FT-IR (Fourier transform infrared spectroscopy) was used as a measuring equipment. Ambient condition of the sample can be exactly controlled by using the ultra-high purity gas supply technology. For example, the moisture and oxygen concentration was easily and exactly controlled. The experiment was carried out using ultra-high purity Ar (argon) gas as a carrier gas. The impurities concentration in Ar gas was below 0.2ppb. Fig.2 shows chemical structure of PTFE (polytetrafluoroethylene) and PFA (tetrafluoroethylene -perfluoroalkoxy ethylene copolymer) investigated in this study. The resin material that consists of F and C (carbon) was selected. The experiment procedure was as follows. At first, the sample was set in the reactor. Then, the Ar gas with the flow rate of 5 cm^3/min was introduced into the reactor, and the sample in the reactor was heated gradually. Heating rate of reactor was 2 ℃/min from 25℃ to 500℃. The released gases from sample by thermal degradation were measured by FT-IR. We evaluated the reactivity of a sample and various metal surfaces by changing the inner surface in the reactor. Fig.3 and Fig.4 shows temperature dependency of PTFE and PFA degradation behavior on various surfaces. The vertical axis shows an absorbance. It is an amount of the released gas from sample by thermal degradation. The horizontal axis shows temperature. The sample was contacted with a) SUS316L-EP surface, b) Al_2O_3 passivation surface, c) TaN surface and d) Ni surface. It was found that the starting temperature of degradation was different. It depended on the kind of the metal surface due to the catalytic effect. As the starting temperature of degradation becomes higher, it is shown that the catalytic effect of metal surface is lower. It was clarified that the Ni surface had the most low-catalytic effect to the fluorocarbon resin. Generally, it is well-known that the Ni surface has catalytic effect. However, it is very interesting that Ni surface does have low-catalytic effect to the fluorocarbon resin. And it was found that the starting temperature of degradation of PFA was lower than PTEF on the same metal surface. It is thought that PFA contains oxygen in structure. Therefore, this result suggests that oxygen in the material accelerates the degradation. From the above obtained results, the optimization of the metal material and removal of oxygen is one of the indispensable parameters to prevent the degradation of the fluorocarbon material in high temperature process. We recommend to adopt Ni for barrier metal of copper interconnection. The improvement of the ULSI devices property such as the yield, the quality, and the reliability can be expected by doing them.

References

[1] F. Pires, M. Papapietro, G. Passemard, P. Noel and O. Demolliens, DUMIC, pp.131-138, Februaly 1997.

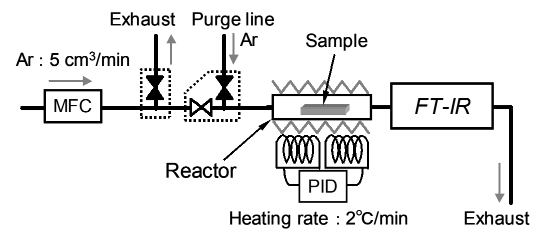

Fig.1 Schematic diagram of experimental setup to analyze the released gases from sample by thermal degradation.

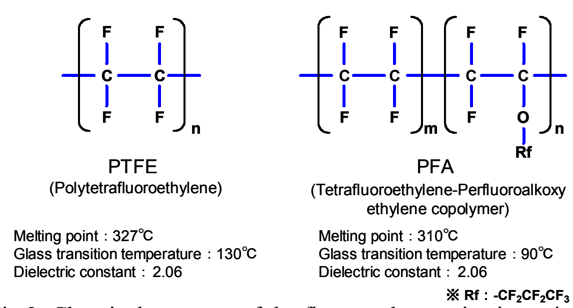

Fig.2 Chemical structure of the fluorocarbon resins investigated in this study.

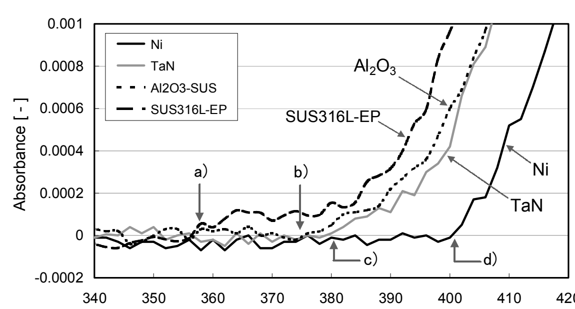

Fig.3 Temperature dependency of PTFE degradation behavior on various surfaces.

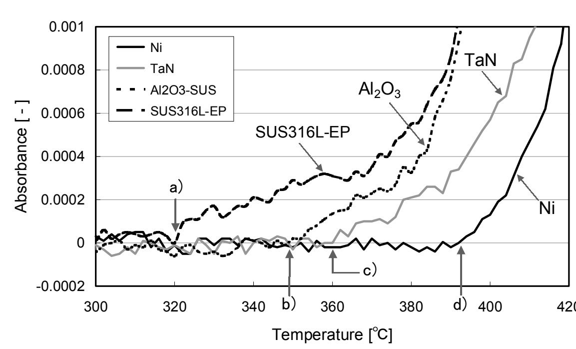

Fig.4 Temperature dependency of PFA degradation behavior on various surfaces.