APPLICATIONS OF PLASMA POLYMERIZATION

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ABSTRACT
Plasma chemistry for organic material in low temperature plasma is given attention in various fields of technical development. The principal processes are organic thin films coating, surface modification and etching of polymeric substrate. In this presentation, an interaction between plasma and polymer will be discussed and the recent development of plasma polymerization will be introduced.

Conventional vinyl polymers are classified into two groups: those that become degraded under high energy irradiation and those that become cross-linked. Polymethylene and polystyrene are known as the polymer become cross-linked, but polymethylmethacrylate is belong to the polymer become degraded. Therefore, the different procedures must be adopted on the processes of polymerization and surface modification for two types of polymer.

Plasma etching phenomena of polymer were studied in two types of reactor with using etching gases O, N, H, and Ar for a cast sheet made from allyl diglicol carbonate (CR-39). Two reactors are a tubular type, which is discharged by parallel plate electrodes and a gas flow type, which is discharged by an induction coil. For both reactors, the etching rate by O plasma was relatively high compared to other gas plasmas, but the difference between etching rate by O plasma and those by other gas plasmas in the tubular type reactor was smaller than those in the gas flow type reactor.

The plasma etched surface was not smooth microscopically. The smoothness depends on the etching gas and the etching conditions. In the gas flow type reactor, the etched surface by O plasma was smooth compared to those by other etching gases. Even if the etching rate was not so large for Ar plasma, numerous pock marks were formed on the etching surface.

As a plasma etching mechanism, physical sputtering and chemical etching are supposed to exist. From the experiments, it is expected that the physical sputtering is a predominant mechanism in the tubular type reactor and the chemical etching is significant in the gas flow type reactor.

Plasma etching rate of degradative polymers is relatively large compared to that of cross-linkable polymers. But the absolute etching rate will be affected by both of molecular structure and constitutive atom ratio in the polymer. The etching rate usually increases with increasing oxygen ratio.

It is supposed that plasma polymerization will be obtained in the competition between deposition and ablation. If the ablative polymer is formed on the substrate, the polymer
deposition was not observed. Whereas the plasma polymerization will be performed when the plasma resistive polymer was formed on the substrate at an energy state in the plasma during plasma polymerization.

Plasma polymerization mechanisms are discussed for two types of reactors. Plasma polymerization in the reactor with parallel plate electrodes is discussed for the gases and discharge parameters in the frequency range between 50 Hz and 13.56 MHz. It was shown that the growth rate showed the peculiar discharge frequency dependence. The frequency dependence of growth rate will be referred to a charge transportation mechanism onto the substrate. The growth rate of ethylene was larger than that of ethane in the observed discharge frequency range. The molecular structure depends on the polymerization condition. At the higher pressure than about 20 Pa, usually soft film was formed. The transparent film was polymerized at about 300 Pa and a small discharge power and the molecular was estimated to be linear small molecules. The yellow film was formed at the lower frequency than about 2 MHz and the molecular was supposed to be highly crosslinked.

A hard and transparant film was obtained on silicon wafers by plasma polymerization of ethane and methane at the lower pressure than about 20 Pa. The C-H bond was negligibly small compared to the film formed at the higher pressure. The refractive index was about 2.4 which was larger than that of conventional polyethylene (about 1.5).

Plasma polymerization in a carrier gas flow type reactor is discussed on its reaction mechanism and characterization of the film. Ionic and radical polymerization were distinguished with NMR measurement of plasma polymerized methylmethacrylate under various carrier gases. Ionic mechanism was predominantly occurred in case of O and SF carrier gas, but radical mechanism was expected to be important for inert gases and at a lower pressure.

Several kinds of application of plasma polymerized films are introduced. Plasma polymerized methyl methacrylate was successfully applied to an electron beam and an X ray resist in a vacuum lithography, all of processes were performed in an unified vacuum system. In order to develop the lithography, the sensitivity and resolution of the resist must be improved markedly. For this purpose, the co-polymer and multilayer resist were proposed as a positive resist and a graft polymerization was also examined as a negative resist. The selection of etching reactor and etching gas was observed to be important for the high resolution development.

By using the gas flow type reactor, plasma polymerized organosilicon was formed for a protective layer on a plastic sheet. Plasma polymerized B-C-N-H compound was also deposited on the plastic sheet in the form of transparent and hard film.