STABILIZATION OF TRICHLOROTRIFLUOROETHANE (CFC-113) BY PLASMA COPOLYMERIZATION WITH A HYDROCARBON MONOMER

Osamu Tsuji, Mikio Sawai, Hirohiko Nakano and Takeshi Minaguchi
SAMCO International Inc. Research center
33, Tanakamiya-cho, Takeda, Fushimi-ku, Kyoto 612, Japan
Theodore Wydeven
Opto Films/SAMCO International
532 Weddell Dr., Suite 5, Sunnyvale, CA 94089, U.S.A.

ABSTRUCT

We carried out the plasma copolymerization and stabilization of trichlorotrifluoroethane (CFC-113) by forming a thin solid film. Plasma homopolymerization of CFC-113 is known to be difficult when done under conventional plasma deposition conditions. However, we found that by mixing it with substances having similar chemical structures, such as ethane (C_2H_6) or ethylene (C_2H_4), it polymerized at a much higher rate. ESCA analysis revealed that fluorine and chlorine in the feed gas was incorporated into the copolymer film. As much as 60 percent of the CFC-113 in the feed gas mixture of CFC-113/C_2H_4 was deposited in the solid copolymer film. The maximum copolymerization rate with C_2H_4 was attained at a mole ratio of approximately 1:1 for CFC-113 and C_2H_4. The copolymerization of CFC-113 with C_2H_4 reached deposition rates up to approximately 35 times the rate of C_2H_4 alone. The deposition rate of the copolymer was dependent on total pressure and RF power. Hydrogen derived from the hydrocarbon in the gas mixture is thought to play an important role in accelerating the deposition rate of the copolymer. It was also confirmed by mass spectroscopy that during the course of the copolymerization reaction, fluorine and chlorine fragments derived from CFC-113 were removed from the plasma gas apparently by copolymerization with the C_2H_4 monomer.

INTRODUCTION

CFCs (Chlorofluorocarbons) have been widely used as refrigerants and cleanig agents, but due to the fact that CFCs also destroy the earth's ozone layer and contribute to global warming, it was written in the Montreal Agreement that for the purpose of environmental protection the use of CFCs shouled, in priciple, be completely eliminated from use throughout the world by the end of 1995. In order to meet this goal, various nations around the world are now actively collecting the remaining CFC reserves. The collected CFCs are then decomposed at high temperature. High temperature decomposition introduces an additional problem, namely, the production of large amounts of strong acids,such as hydrofluoric acid (HCl), which can enter and further pollute the environment. In addition, high temperature decomposition requires a considerable amount of thermal energy, making it a very high cost disposal method. In our research, we carried out the plasma copolymerization and stabilization of CFC-113 (trichlorotrifluoroethane) by forming a thin solid film.[1,2] The copolymerization and stabilization process involved mixing the CFC-113 vapor during plasma deposition with substances having similar chemical structures, such as C_2H_4 or C_2H_6.

EXPERIMENTAL

Monomers

CFC-113 is a halogenated compound that in recent years has been used in large quantities as a solvent for cleaning purposes. The chemical structure is the same as ethane except that the hydrogen atoms have been exchanged for three fluorine and chlorine atoms. CFC-113 is a stable and non-flammable compound, making it very convenient for use in industry. The specific gravity is 1.576, the vapor pressure is 273 mmHg, the ozone layer destructive coefficient is 0.8, and the global warming coefficients is 1.3-1.4. In comparison with other cleaning solvents, CFC-113 has a relatively large effect on damage to the environment. The CFC-113 used for our experiments was provided by Mitsui Fluorochemical, and was stored in a 200 ml metal vessel attached to the plasma reactor. Monomer vapor from the storae vessel flowed through a mass flow controller and into the plasma reaction chamber. As a source gas for copolymerization, we used either C_2H_4 or C_2H_6, i.e., hydrocarbons with chemical structures similar to CFC-113. As is well know in plasma chemistry, C_2H_4 which contains a double bond (C=C) is easily disassociated in a plasma and therefore easy to use in plasma homopolymerization.

For this reason, we used C_2H_4 and CFC-113 for copolymerization in most of our experiments. The C_2H_4 source gas was stored in a 10 liter vessel and contained a few ppm of hydrogen which was not removed for the experiments reported here. Ethylene flow rate into the plasma reactor was also controlled by a mass flow controller.

Instruments

The plasma reactor used for our experiments is configured with parallel-plate electrodes and capacitively-coupled through a matching network to a 13.56 MHz radio frequency power supply. The substrate diameter is 160 mm, and the bell-jar is made from srainless steel (SUS 304). Figure 1 shows configuration of the plasma deposition system. We inserted an orifice directly above the lower electrode for sampling the plasma gas by mass spectroscopy. The orifice and attached inlet line were connected to a quadrupole mass spectrometer (Anelva, Model AGA-100) analysis. The evacuation system used for the plasma reactor consisted of a mechanical booster pump (100 m^3/hr) and a mechanical ratary pump (0.3 m^3/min). A cold trap made of Pyrex™ glass was installed between the reactor and the mechanical booster pump in order to trap by-products of the reaction. Fomblin™ oil was used in the rotary pump. The plasma copolymer was deposited on the surface of 4" diameter silicon wafers. The thickness of the polymer deposited on the silicon wafer was determined by measuring the height of a step on the wafer with a Dek-Tak Model 3030 thickness monitor. Film density was calculated by using the film weight (measured with a microbalance manufactured by CHYO Balance Corp., Model JPN-200W) thickness and area. Surface analysis of the films for fluorine and chlorine was done by ESCA using a

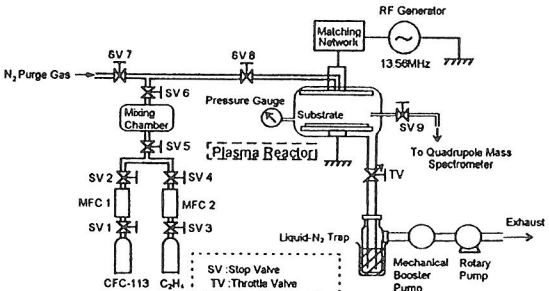

FIG.1. Schematic diagram of the plasma reactor and associated instrumentation.

Shimazu ESCA-750 spectrometer. Carbon and hydrogen content of the polymers was determined using a Yanaco Model MT-3 CHN analyzer.

RESULT AND DISCUSSION

Deposition Rate of Plasma Copolymers

Figure 2 shows the deposition rate of the plasma polymer formed at various mole ratio of CFC-113 and C_2H_4 reactants in the feed gas. The parameters used to acquire the data shown in Figure 2 were : RF power = 100 Watts, Pressure = 0.4 Torr, Total flow rate of CFC-113 + C_2H_4 = 40 SCCM.

Most noteworthy in Figure 2 is the high polymer deposition rate at a CFC-113/C_2H_4 mole ratio of approximately 1:1. The deposition rate of C_2H_4 alone is only 0.3-0.5 nm/sec, which is comparable to the rate for most plasma polymers. On the other hand, we show on the right side of Figure 2, when only CFC-113 is used, the apparent deposition rate shifts to the minus side, indicating that plasma etching of the silicon substrate rather than deposition is taking place. However, when CFC-113 is mixed with C_2H_4 and then plasma polymerized, the deposition rate is 35 times faster than with C_2H_4 alone.[3] Figure 3 shows the deposition rate of the plasma polymer at a 1:1 mole ratio of CFC-113 to C_2H_4 in the feed gas mixture versus total pressure. We obtained a maximum deposition rate of approximately 14 nm/sec at the highest pressure shown. Figure 4 shows the dependency deposition rate on r.f. power, also at a 1:1 mole ratio of CFC-113 to C_2H_4 in the feed gas mixture. This figure shows that the deposition rate increase as a function of r.f. power up to about 100 Watts while beyond this power the deposition rate decreases. This phenomenon is often observed in plasma polymerization reactions when fluorine is present.[4,5] From the results we conclude that in order to attain a maximum copolymer deposition rate, total pressure and r.f. power must be optimized. In order to calculate recovery, we used the measured mass flow rate of plasma

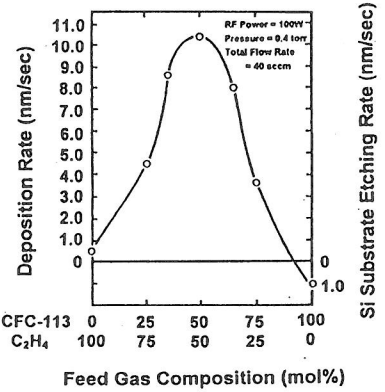

FIG. 2. The deposition rate of CFC-113/C_2H_4 copolymer versus the mol ratio of reactants in the feed gas mixture.

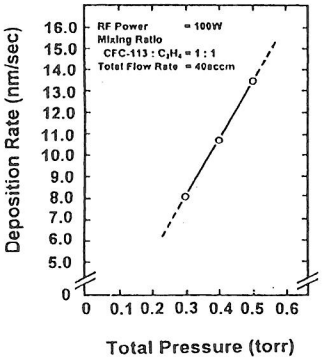

FIG. 3. Variation of deposition rate of the plasma polymer with total pressure in the reaction chamber at a CFC-113 : C_2H_4 mol ratio of 1 : 1.

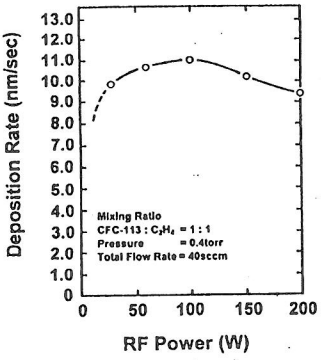

FIG. 4. Variation of deposition rate of the plasma polymer with RF power at a CFC-113 : C_2H_4 mol ratio of 1 : 1.

copolymer scraped from the upper and lower electrodes of the plasma reactor after 10 minutes of deposition. The amount of gas flowing into the reactor was then compared with the amount of polymer collected from the upper and lower electrodes. The recovery increased with the reactor pressure in the range 0.3 to 0.5 Torr. Recovery was about 40 percent at a total pressure of 0.3 Torr and 55 percent at a total pressure of 0.5 Torr.

Density

The polymer resulting from the plasma polymerization of CFC-113 and C_2H_4 can be considered to be an amorphous structure having a density between that of CFC-113 and C_2H_4 homopolymers. In order to confirm the copolymer density, we deposited on 4" silicon wafers 10 μ m thick films at various CFC-113:C_2H_4 mole ratios. Film density was then calculated from the thickness wafer area and weight of the films.[6] Figure 5 shows the variation in plasma copolymer density with composition of the feed gas. Also shown in Figure 5 for comparison purpose are the densities of the conventional polymers of high density polyethylene and polychlorotrifluoroethylene.[7] The higher density of the plasma copolymers relative to high density polyethylene suggests that CFC-113 was incorpolated into the plasma copolymer.

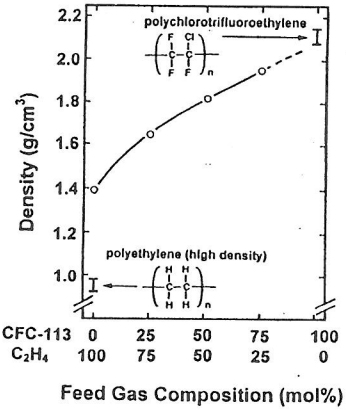

FIG. 5. The density of the CFC-113/C_2H_4 copolymer versus the mol ratio of CFC-113 to C_2H_4 in the feed gas.

XPS Analysis

We carried out XPS analysis of some plasma copolymers deposited on pieces of silicon wafers in order to identify functional groups in the plasma copolymer and determine the amounts of fuorine and chlorine in the film. For these experiments the CFC-113:C_2H_4 mole ratio was held constant at 1:1 and the plasma polymer film were deposited at different power levels. Deconvolution of XPS spectra showned not only C-H but also C-F, C-F_2, C-Cl, C-Cl_2, C-ClF,C-Cl_2F, C-ClF_2 functionalities. Figure 6 shows that while at a low r.f. power level, 25 Watts, the concentration of fluorine in the film surface is approximately double that of chlorine while at an r.f. power of 200 Watts, both elements have approximately the same concentrations, 30 atom % each. Figure 6 also shows that the chlorine concentration remains relatively constant while the fluorine concentration decreases with increasing r.f. power.

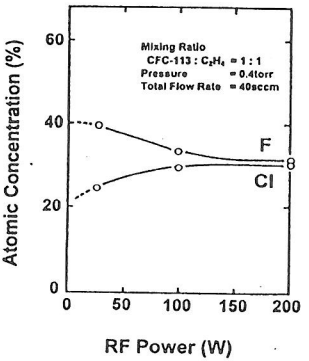

FIG. 6. Atomic percent of F and Cl in the copolymer derived from CFC-113 and C_2H_4 versus RF power determined by XPS.

Elemental Analysis

For elemental analysis of the plasma polymer formed from a 1:1 mixture of CFC-113 and C_2H_4, we scaped from the surface of a silicon wafer 2-3 mg of the polymer and analysed it for carbon, hydrogen and residue. The analysis for carbon and hydrogen (the average of two measurements) was C=31.30% and H=0.75%. The residue was presumed to be Cl+F=67.95%. From the elemental analysis we calculate the number of gram atoms of the elements to be : C=31.30/12.01=2.61; H=0.75/1.008=0.74; and Cl+F=67.95/(35.45+19.00)=1.25. Therefore, the empirical formula for the plasma copolymer prepared from a 1:1 mixture of CFC-113 and C_2H_4 is $C_{2.61}H_{0.74}Cl_{1.25}F_{1.25}$, assuming equal number of chlorine and fluorine atoms in the copolymer. The latter assumption appeared reasonable based on our ESCA data. If we now compare the empirical formula with the formula expected for the copolymer by assuming a 1:1 ratio of CFC-113 to C_2H_4 ($C_2H_4Cl_3F_3$) in the copolymer, we see that the copolymer is very deficient in hydrogen and some what less deficient in Cl and F. The mass spectrum shown later also provides support for the concept that significant dehydrogenation occurs during plasma copolymerization of CFC-113 and C_2H_4.

Reaction Process Monitoring by Mass Spectroscopy

In order to further investigate the plasma copolymerization reaction, we inserted a small orifice near the lower electrodes of the plasma reactor to gather plasma species (ions) for analysis by mass spectroscopy. Figure 7- (I) shows the mass spectrum of the plasma species observed when only CFC-113 is present as a reactant. The primary plasma species found in this case were CF, Cl, HCl, CCl, CF_2, CClF, $CClF_2$, and trace amounts of species such as F, F_2 and HF. Figure 7-(II) shows the mass spectrum taken when CFC-113 and C_2H_4 are present in a 1:1 mole ratio in the feed gas. It can be seen from spectrum that the C_2H_4 causes several of the halocarbon species, in particular CF, CCl, CClF and $CClF_2$ to decrease to very low concentrations. It is also interesting to note that CF_2 is the only halocarbon species that increases in concentration after the addition of C_2H_4. The decrease in concentration of most of the halocarbon species upon addition of C_2H_4 provides avidence that these species are removed from the plasma when C_2H_4 is present and may have been part of the plasma copolymer. The high intensity of the H and H_2 peaks in Figure 7- (II) also shows that during the course of the copolymerization reaction, extensive dehydrogenation occurs. Inagaki et al.,[8] in their study of plasma polymerization of perfluorobenzene and pentafluorobenzene found that pentafluorobenzene polymeized faster than perfluorobenzene. These authors described the enhanced etch rate of pentafluorobenzene to the presence of the hydrogen atom in this monomer. The enhanced etch

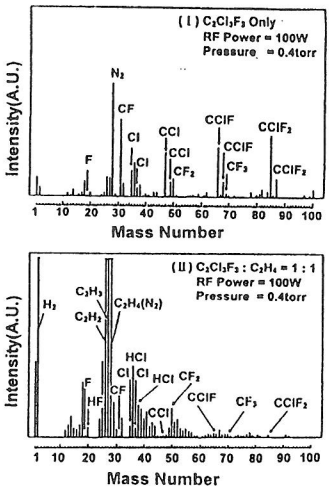

FIG. 7. Mass spectra of ions found in the plasma gases of CFC-113 only (I) and CFC-113/C_2H_4 (II).

rate of our mixtures relative to homopolymerization of the reactants may also be due to hydrogen derived from the hydrocarbon co-reactant.

CONCLUSIONS

The rate of plasma polymerization of CFC-113 was greatly enhanced by mixing it with a hydrocarbon monomer, such as ethylene, during deposition. The maximum deposition rate for forming the plasma copolymer occurred at a CFC-113 to C_2H_4 mole ratio of 1:1. The enhanced deposition rate of CFC-113 in the presence of a hydrocarbon may be due to hydrogen derived from fluorine and HF reacts with the hydrocarbon. The plasma polymer formed by copolymerization of CFC-113 and ethylene at a mole ratio of 1:1 incorporated as much as 60% of the Cl and F in the reactant gas mixture. The empitical formula for the plasma copolymer derived from elemental analysis is $C_{2.61}H_{0.74}Cl_{1.25}F_{1.25}$. The plasma copolymerization process described here may be useful method for disposing of compounds harmful to the environment such as CFC-113.

REFERENCES

1) O. Tsuji, M. Sawai, H. Nakano and K. Miyashiata; 7th Symposium on Plasma Materials Conference, Abstruct P. 48 (1994).
2) O. Tsuji, M. Sawai, H. Nakano and T. Minaguchi; "Chemical Instruments" 73, Feb (1995)
3) O. Tsuji, M. Sawai, H. Nakano and T. Minaguchi; Paper submitted for the J. Photopolymer Sci. and Technology (1995)
4) O. Tsuji, M. Sawai, H. Nakano and T. Minaguchi; 8th symposium on Plasma Materials conference, Abstruct (1995)
5) H. Kobayashi, A.T. Bell and M. Shen; Macromolecules 7, 277 (1974).
6) M.A. Golub, T. Wydeven and R.D. Cormia; J. Polym. Sci.: Part A. polym. Chem.,30, 2683 (1992).
7) Chimistry Handbook, Japan Chemical Society, P.528.
8) N. Inagaki, N. Kobayashi and M. Matsushima; J. Membrane Sci., 38, 85-93 (1988).