PRESSURE DEPENDENCE OF DISCHARGE BY-PRODUCTS FROM Ar-CH_4-H_2 AND Ar-CO_2-H_2 MIXTURE ICP PLASMAS

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ABSTRACT

Pressure dependence of discharge by products from Ar-CH_4-H_2 and Ar-CO_2-H_2 mixture ICP plasmas is experimentally investigated. The results show that the formation of a C, CH_x and C_yH_z hydrocarbons in both gas mixtures. However, thin film or solid products are only observed under narrow operating conditions for the Ar-CH_4-H_2 system, and the Ar-CO_2-H_2 system was observed to be acting as an etching or ashing gas to the solid products.

INTRODUCTION

Dissociation of CO_2, and CH_4 by thermal plasmas is important for the development of reforming gas production in metallurgical applications and in diamond synthesis. In this work, an experimental investigation has been conducted to identify discharge by-products in the forms of gas and solid products for Ar-CH_4-H_2 and Ar-CO_2-H_2 mixture gas plasmas under the wide range of gas pressure.

EXPERIMENTAL APPARATUS

Experiments were conducted using a RF inductive coupled plasma torch (ICP) for the gas pressure from 0.1 to 500 torr, the RF power from 0.1 to

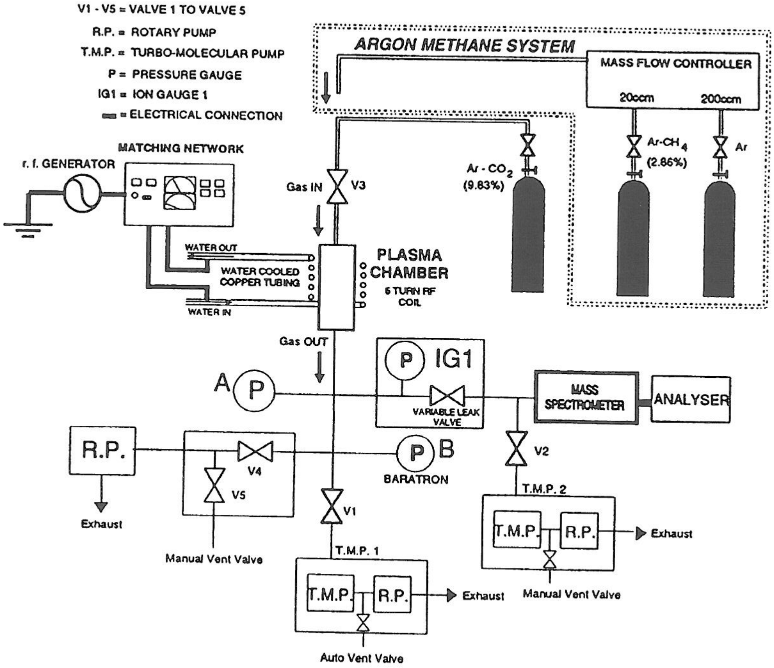

Fig. 1 Schematics of experimental set-up.

1.5 KW, and the percentage mixture of CH_4-H_2 or CO_2-H_2 from 0.5 to 10%. Schematics of experimental apparatus used in shown in Fig. 1. Plasma is generated by 27 MHz, 2.5 kW RF power supply, matching units, and water cooled coils. Pure and mixture gases are introduced from the side of the reaction chamber and through the plasma ignitors via gas flow meter. The plasma ignitor is consists of a hollow electrode inside ceramic tubes as shown in Fig. 2. The neutral gas species were determined by a mass spectrometer, and the plasma parameters are determined by electrostatic probes. The solid products deposited to the aluminum or silicone substrates (Fig. 2) are analyzed by the X-ray diffraction, SEM, FTIR and Auger spectroscopy.

GASEOUS PRODUCTS

During the experiments, no stable gas compositions have been observed during the ICP discharge. Typical Ar-CH_4-H_2 plasma gas compositions before and during ICP discharges are shown in Fig. 3. Before discharge, gas compositions are Ar, CH_4 and H_2, hence Ar^+ (40), Ar^{++} (20), CH_4^+ (16), H_2^+ (2), H^+ (1), CH_3^+ (15), C^+ (12) and CH_2^+ (14) are observed due to the electron impact dissociative ionization in a mass spectrometer.

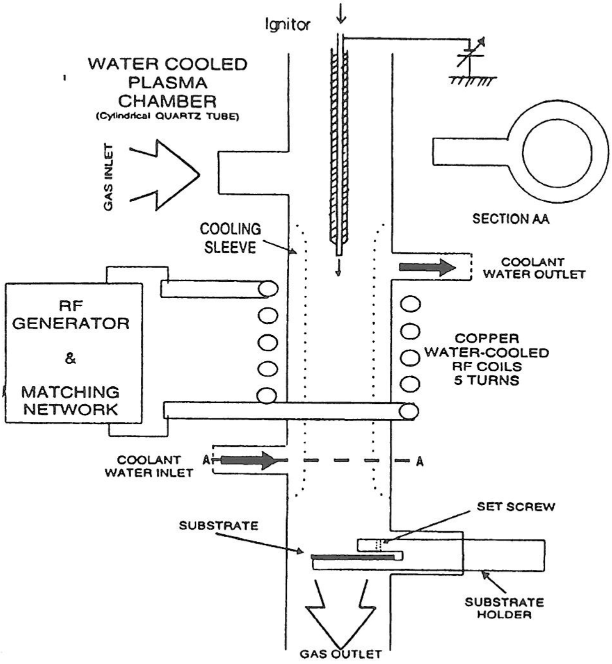

Fig. 2 Schematics of discharge tube and plasma ignitor

However, during ICP discharges, these molecules are dissociated in plasma to form various radicals and larger molecules [2]. Figures 2a and 2b show that the discharge by-products are time-dependent and much larger mass, such as $C_2H_4^+$, $C_2H_8^+$, $C_3H_7^+$, $C_3H_8^+$, $C_4H_{10}^+$ etc. are produced.

Typical discharge by-products observed for the Ar-CO_2-H_2 system is shown in Fig. 3. As expected from neutral composition before ICP discharges, Ar^+ (40), Ar^{++} (20), H_2^+ (2), H^+ (1), CO_2^+ (44), CO^+ (28), O^+ (16), and O_2^+ (32) are observed. However, after ICP discharge, significant amounts of hydrocarbons [1] are also observed. Significant amounts of carbons C^+ (12) and C_3^+ (36) are also observed.

SOLID BY-PRODUCTS

For Ar-CO_2 systems, the typical Auger spectrum on the surface of Al substrates shows that the part of the ICP plasma dissociated carbon is implanted to the Al surface.

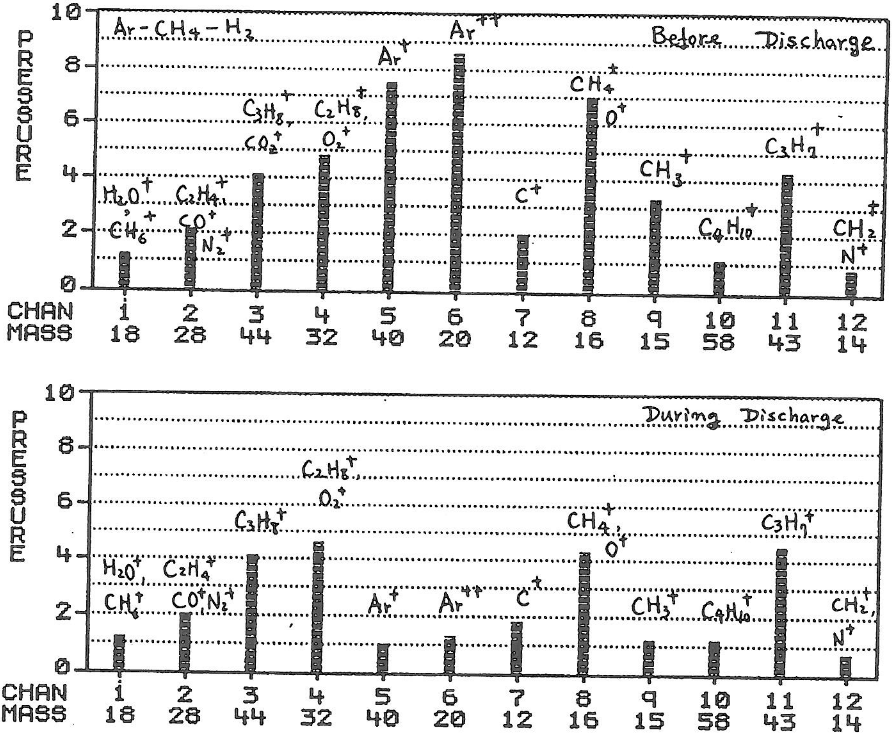

Fig. 3 Typical Ar-CO_2-H_2 plasma gas compositions before and during ICP discharges for P = 20 Torr, RF power 0.5 kW, and ($Ar : CH_4 : H_2 = 92.6 : 1.1 : 6.3$).

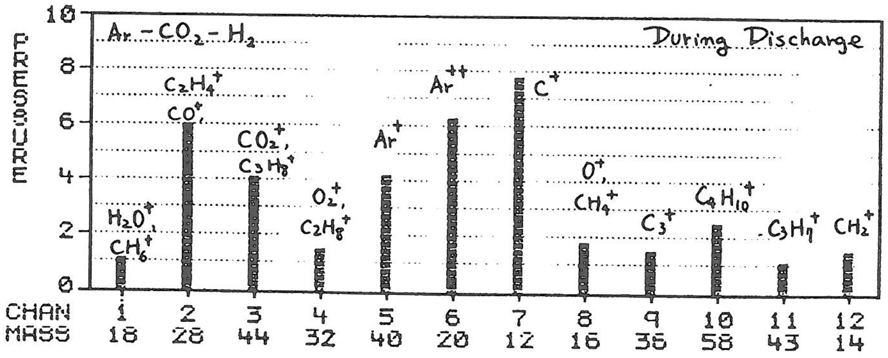

Fig. 4 Typical Ar-CO_2-H_2 plasma gas compositions before and during ICP discharges for P = 0.83 Torr, RF power 0.61 kW, and ($Ar : CH_4 : H_2 = 90 : 5 : 5$).

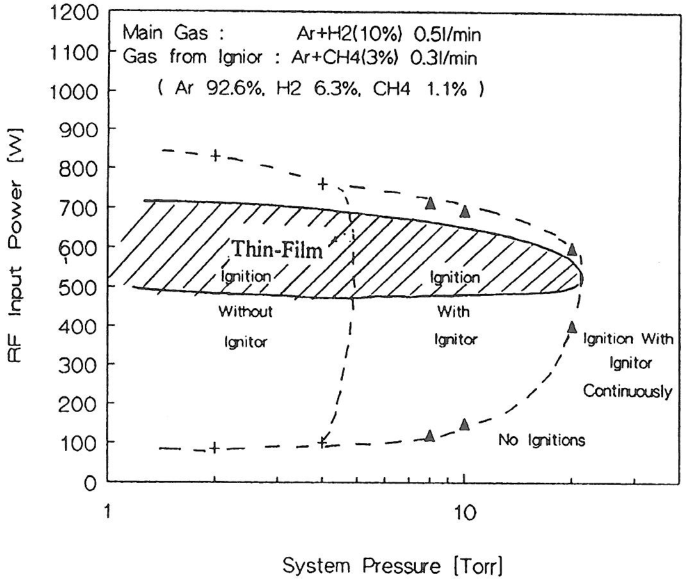

Fig. 5 The discharge pattern map and the region where the thin film depositions are observed for Ar-CO_2-H_2 mixture gas ICP plasmas.

For the Ar-CH_4-H_2 and Ar-CH_4 systems, the thin film is only formed under the conditions as shown in Fig. 5. From the SEM, FTIR and X-ray diffraction observations, amorphous carbon, polymer, diamond or their mixture are observed in thin films.

For the Ar-CO_2-H_2 system, no thin film formation is observed. However, the thin films formed by Ar-CH_4-H_2 systems in the discharge tube wall are removed within a few minutes of an ICP plasma discharge operation under this mixture. Hence, this type plasma can be used as plasma etchings or ashings.

CONCLUDING REMARKS

An experimental investigation has been conducted to study discharge by-products under Ar-CH_4-H_2 and Ar-CO_2-H_2 gas mixture ICP plasmas.

The results show that: (1) the mass numbers of 12, 14, 15, 16, 17, 18, 20, 27, 28, 29, 32, 36, 39, 40, 43, 44, 58, 105 were observed; (2) C, CH_4, C_2H_6, C_4H_{10}, and C_3H_8 are identified as a stable final product for Ar-CH_4-H_2 gas mixtures; (3) spherical particles are observed uniformly distributed on the surface of thin films; (4) deposited carbon thin films are gasified under a few minutes of Ar-CO_2-H_2 plasma discharge environment; and (5) formation of hydrocarbon compounds is observed in Ar-CO_2-H_2 gas mixtures.

ACKNOWLEDGEMENTS

The authors wish to thank H. Yoshioka, S. Ono and S. Teii for their valuable discussions and comments. This work is supported partly by Ebara Co. and the National Science and Engineering Research Council of Canada (JSC, CD, CD, DCL.).

REFERENCES

1. J.S. Chang and T.G. Beuthe, J. High Temp. Chem. Proc., 1, 333-341 (1992).

2. J.S. Chang, H. Kohno, W. He, A.A. Berezin, P.C. Looy, K. Iijima, S. Honda and A. Shibuya, Acta Physica U.C., 35, 59-67, 1994.