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Corrosion-Resistant Coatings for High-Temperature High-Sulfur-Activity Applications

Final Report

J.R. Selman, B. Aladjov, and B. Chen

January 1992

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CORROSION-RESISTANT COATINGS FOR HIGH-TEMPERATURE HIGH-SULFUR-ACTIVITY APPLICATIONS

Final Report

January 1992

by

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S U M M A R Y

Task 1. Optimized Deposition of Molybdenum and Molybdenum Carbide by Molten Salt Electrochemical Deposition

During the period covered by this report, the previously started experiments to verify the feasibility of obtaining molybdenum and molybdenum carbide coatings from oxide-based melts were continued. In the ongoing experiments a molten salt bath consisting of an equimolar mixture of Na_2WO_4 and K_2WO_4 was used. The molybdenum and carbon species were introduced as alkali molybdate and carbonate. Results thus far indicate that the coating morphology depends strongly on melt composition, temperature and moisture content. Application of initial pre-electrolysis significantly changes the composition and morphology of the coatings. Using non-lithium alkali salts, coatings of better quality were obtained. In recent experiments, adding 3-8 mol% $Na_2B_4O_7$ to the basic non-lithium bath composition was observed to cause significant morphology and quality changes. Results thus far show that these bath compositions produce a more uniform small-grain-size coating, moreover they do not require extensive purification. Both constant current and reverse and/or pulse current patterns were applied during plating. The latter produces smaller-grain-size coatings than the former at the same working temperature.

Task 2. Preparation of Mo and Mo_2C by Plasma Enhanced Chemical Vapor Deposition (PECVD)

Continuing an earlier reported effort, research was undertaken to deposit Mo and Mo_2C films on a substrate of 2.54 cm (1-in) by 3.81 cm (1.5-in) area. Using an orthogonal factorial design, a new series of experiments has been carried out to investigate the effect of the evaporation rate of $Mo(CO)_6$ as a precursor. The PECVD procedure has been improved to minimize losses of $Mo(CO)_6$ in transport to the reaction chamber. From the weight gain of the substrate, initial conclusions have been drawn about the optimal conditions for maximum evaporation rate, deposition rate and thickness. Thicker coatings, of up to a few μm thickness, have been obtained which show two different types of crystallites growing on an initially amorphous film. A two-dimensional transport and reaction kinetics model for a parallel-plate PECVD reactor was outlined. The PECVD results will be used to verify the model, after further additions and refinements. The primary parameters to be explored are those representing the deposition kinetics of Mo and C. Further experiments and analysis are in progress.

Corrosion-Resistant Coatings for High-Temperature High-Sulfur-Activity Applications

REPORT

Task 1. Optimized Deposition of Molybdenum and Molybdenum Carbide by Molten Salt Electrochemical Deposition.

INTRODUCTION

This research effort is aimed at advancing the fabrication (preparation) and characterization of coatings of molybdenum and molybdenum carbide by molten salt electrochemical deposition (MSECD) and plasma enhanced chemical vapor deposition (PECVD). These coatings are considered candidate materials for coating the container and positive-electrode current collector substrates of high-temperature batteries such as the sodium-sulfur and lithium-FeS_2 batteries.

Sodium and lithium polysulfides melts are extremely corrosive and selection of a material for the current collector and container is one of the most important challenges in the successful development of high energy metal/sulfide electrochemical power sources.

For such batteries to have an acceptable cell life, any material used for the current collector and container should possess very high corrosion resistance, should not be reduced by sodium or lithium, and should have a high electrical conductivity. Other important requirements are ease of fabrication, mechanical strength, low weight and low cost (1).

A large number of different corrosion tests have been conducted on numerous materials (metals, alloys, inorganic materials and some protective coatings on corrodible substrates) with the aim to identify an acceptable current collector and case material for the positive electrode (2,3,4). These tests include both static and dynamic in-cell tests at various melt compositions and temperatures.

Only a few materials have been found to satisfy these requirements. The materials in question are aluminum, chromium, molybdenum, some special high-chromium based alloys and some composite materials such as metal carbides. The corrosion behavior of these materials is summarized in the following.

1. Aluminum forms a thin stable film of Al_2S_3 (5), which has a high electrical resistivity, so it cannot, by itself, be used as current collector, however, molybdenum-coated aluminum appears to offer a suitable combination of corrosion resistance and conductivity;

2. Chromium forms a layer of Cr_2S_3 with an acceptably low rate of corrosion. It was found that the solubility of Cr_2S_3 in sodium polysulfides is much lower than that of the sulfides of iron, copper, nickel etc.(6);

3. Molybdenum forms a thin stable layer of MoS_2 which is electronically conducting. From this, and from numerous in-cell tests, it has been concluded that molybdenum offers excellent corrosion protection (7,8,9).

Mo metal has good physical properties at moderately high temperatures and excellent corrosion resistance against molten salts. However, as a bulk material it is very expensive and poorly machinable.

The above materials nevertheless cannot completely satisfy all of the above noted requirements e.g., ease of fabrication at relatively low cost. Therefore, the efforts of scientists and manufacturers are directed, at present, mainly toward new materials as well as new and efficient processes. In the latter case, the objective is to produce those materials which have shown an adequate degree of corrosion resistance in the form of coatings on corrodible substrates.

In the present project we aim to explore MSECD and PECVD as methods to produce dense coatings of molybdenum and molybdenum carbide. MSECD is a powerful method which can be used to produce various compound-based coatings having improved properties compared with those of the pure single chemical elements. This method offers the ability to coat complex shapes and provides good process control by making use of current/potential variation.

BACKGROUND

Formation of refractory metal carbide deposits by MSECD using several different bath composition (chloride, chloride-oxide, fluoride, oxide) has been demonstrated by many authors (10-14). Recently Soviet scientists (15-18) proposed a method of non-fluoride based electrochemical deposition from a melt consisting completely of oxides, with air as ambient atmosphere.

The method can be summarized as follows. Mo_2C coatings are deposited directly on mild steel from a Na_2WO_4-K_2WO_4-Li_2MoO_4-Li_2CO_3 melt at 900 °C. Dense coatings with a thickness of up to 50 μm are obtained at cathodic current densities between 20 and 100 mA/cm^2. The Faradaic efficiency calculated on the basis of 16 electrons/molecule Mo_2C is between 35 and 50 %.

The authors assumed that in Na_2WO_4 - K_2WO_4 melts which contain Li_2CO_3 and Li_2MoO_4 the following equilibria exist:

$$CO_3^{2-} + xLi^+ \rightleftharpoons \{ Li_x^+[CO_3^{2-}] \}^{x-2} \rightleftharpoons Li_xO^{x-2} + CO_2 \quad (1)$$

$$MoO_4^{2-} + xLi^+ \rightleftharpoons \{ Li_x^+[MoO_4^{2-}] \}^{x-2} \quad (2)$$

During electrochemical deposition two parallel cathodic reduction processes take place:

$$3CO_2 + 4e^- \rightarrow C + 2CO_3^{2-} \quad (3)$$

$$\{ Li_x^+[MoO_4^{2-}] \}^{x-2} + 6e^- \rightarrow Mo + \frac{x}{2}Li_2O + (4-\frac{x}{2})O^{2-} \quad (4)$$

Followed by the reaction of molybdenum and carbon to form Mo_2C.

The authors attribute the deposition of Mo_2C from oxide melts to the instantaneous reaction of carbon and molybdenum produced from the corresponding oxygenated anions. As a result of this reaction a compact pore-free deposit of molybdenum carbide is obtained with good adhesion to the low carbon steel substrate.

Using the same method, the above mentioned authors also obtained Mo_2C+W coatings by electrochemical deposition of tungsten, at a cathodic current density of about 50 mA/cm^2, from a Na_2WO_4-Li_2WO_4-WO_3 melt at about 850 °C on samples precoated with Mo_2C.

Preliminary results on the corrosion and electrochemical behavior of Mo_2C coatings deposited electrochemically on low carbon steel show good promise for corrosion protection of the cathode container in lithium/iron sulfide and sodium/sulfur batteries (19). These results agree with those obtained earlier in this project, when Mo_2C coatings were exposed to Na_2S_4 melts (20).

EXPERIMENTAL

During the period covered by this report, the previously started experiments to verify the feasibility of obtaining Mo_2C coatings from oxide based melt were continued.

The conditions for MSECD from fluoride and oxide baths are shown in Table 1. Initially, our research efforts were directed mainly to produce dense and pore-free molybdenum carbide coatings on low carbon steel. It was our objective also to determine some correlations with process parameters such as temperature, current density, melt composition, as well as to compare the quality and morphology of the molybdenum carbide coatings produced from the fluoride and oxide electrolyte baths.

In the ongoing experiments a molten bath consisting of an equimolar mixture of Na_2WO_4 and K_2WO_4 was used. The molybdenum and carbon species were introduced as alkali molybdate and carbonate, by direct mixing with the base tungstates as a powder.

1. Electrodes:

    1.1. Cathodes:

Cylindrical cathodes with 3.1 or 6.3 mm dia and about 30 mm length were cut from a low-carbon steel rod (AISI 1018). Each cathode substrate was screwed or compressed into a long

low-carbon steel holder of 6.3 mm dia to ensure excellent electrical connection.
The cathodes were initially etched with 10% hydrochloric acid followed by rapid rinsing by water and acetone. Later, they were cleaned mechanically using successively finer grades of silicon carbide paper (240, 320, 400, 600), and then rinsed again by alcohol and water. Next, in most cases, they were polished with Alfa Micropolish Alumina Solution - 1.0 μm (Buehler), followed by a final ultrasonication in alcohol and acetone.

To check the deposit morphology and adhesion to a low carbon steel substrate, several coatings were deposited on a nickel interlayer which was first plated onto the substrate at room temperature from a Watts bath. The main purpose of the nickel interlayer is to avoid direct contact of the molten bath with the iron substrate, which may cause poor deposit adhesion. The bath composition was:

Nickel sulfate, cryst.$7H_2O$	400 g/l
Nickel chloride, cryst.$6H_2O$	50 g/l
Boric acid	35 g/l
Sodium lauryl sulfate	1 g/l

1.2. Anodes:

The anodes were pure metallic molybdenum or carbon rod of 6.3 mm dia. They were installed as the central electrode of the electrochemical cell assembly. The molybdenum anodes were initially chemically treated for about 1 hour in a solution of hydrogen peroxide and isopropanol in water. Later, they were in some cases anodically electropolished for 1-2 minutes at room temperature in a solution of phosphoric acid and sulfuric acid.

Regardless of the anode material used, the anodic process in both cases includes the following reaction.

$$CO_3^{2-} = CO_2 + \frac{1}{2}O_2 + 2e^- \qquad (5)$$

This interferes with the dissolution of the molybdenum anode, which also serves as a source of molybdenum ions. At this high working temperature (above 600 °C) in the presence of air and oxygen, the molybdenum anodes oxidize to form a mixture of molybdenum oxides.

2. Electrochemical Plating Cell:

The electrochemical plating cell assembly is schematically presented in Figure 1. It consists of an α - Al_2O_3 crucible positioned on the bottom of an electroresistance furnace, a cover of thermo-insulating material with holes for the anode electrodes, a low carbon steel cathode, a platinum flag as quasi-reference electrode, and a chromel-alumel thermocouple. The electrodes and thermocouple passed through the holes of the cover and were immersed in the molten electrolyte melt which occupied the bulk of the crucible. A small Hoskins (Model FD 101) electric furnace was used to fuse the electrolyte and ensure the necessary working temperature.

3. Electrolytes:

3.1 Preparation:

Initially all individual components were dried at 200 - 300 °C for 2 - 3 hours in order to remove as much moisture as possible from the commercially available laboratory chemicals. The pre-dried melt components were weighed and mixed to give the desired electrolyte composition (total quantity usually about 60 g), they were then transferred to the crucible and placed in the furnace. It should be noted that our starting experiments were performed with pre-dried chemicals without any additional purification, therefore many of the early deposits were of poorer quality and adhesion than the later ones.

3.2 Pre-electrolysis:

As a second step, an additional electrochemical purification was carried out. The melt was electrolyzed at about 1.5-2.0 V at 650 °C between two carbon electrodes until the current dropped to a low constant value, in order to remove the remaining moisture completely.

4. Experimental procedure:

After placing the crucible with the dried powder mixture in the furnace, the temperature was raised slowly to 600 °C at which point the electrolyte started to melt. One to two hours were necessary after melting to produce a clear melt. After melting, the temperature of the electrolyte was raised to 650 °C, the carbon electrodes for pre-electrolysis were positioned above the crucible, and after thermal equilibration they were very slowly immersed. The pre-electrolysis electrodes were removed immediately after completion of pre-electrolysis. The plating electrodes were then immediately positioned above the crucible, and after some additional equilibration, they were very slowly immersed in the molten electrolyte to avoid thermal shock. After reaching thermal equilibrium (usually in 1-1.5 hours), the temperature was raised again very slowly to the working temperature, 900 °C. Electrolysis was started within 1 hour after reaching this temperature.

Following electrolysis the temperature was decreased again very slowly, and at 600°C the electrode assembly was removed. After complete cool-down, the electrodes were ultrasonically stripped of adherent frozen melt. In some cases, in order to etch the molybdenum carbide coating, the cathodes were treated for 1-2 min by Murakami reagent which consists of 5 g KOH and 5 g $K_3Fe(CN)_6$ in 50 ml distilled water.

5. Examination of Deposits:

A quick preliminary qualitative test for the presence of pores in the coatings was applied, by reaction with $K_3Fe(CN)_6$ solution. A piece of filter paper, soaked in this solution and placed on the surface of the samples, will show a blue discoloration where the coating has pores or cracks. Microscopic examination of the coating at the sample surface was carried out to assess the morphology, continuity and density of the coating. The surface and metallurgical cross-sections of the coating/substrate were examined by optical microscopy, SEM and X-ray EDS (energy dispersive spectroscopy).

RESULTS AND DISCUSSION

In these experiments the electrolyte bath composition was varied to study the influence of the kind and amount of alkali molybdate and carbonate on the deposits, and to choose, on this basis the optimal composition. Later, the process parameters of molybdenum and Mo_2C deposition from a fixed bath composition were studied to generate coatings with reproducible surface topology and thickness.

1. Bath composition:

Thus far several different bath composition have been utilized with approximately 8 - 10 mol% alkali molybdate and variable amounts of alkali carbonate. Table 2 lists the chemical composition of the electrolyte baths used. According to our previous experiments it appeared that the base electrolyte mixture with additions of lithium molybdate and lithium carbonate produced the best deposits. As pointed out earlier, these experiments, which were performed without pre-electrolysis of the electrolyte, gave in most cases unreproducible results. After pre-electrolysis, coatings of a more reproducible quality were obtained.

Using non-lithium alkali molybdates and carbonates, coatings of an even better quality were obtained. In recent experiments, adding 3-8 mol% $Na_2B_4O_7$ to the basic non-lithium bath composition was observed to cause significant morphology and quality changes. Results thus far show that these bath compositions produce a more uniform small-grain-size coating, moreover they do not require extensive purification because they are apparently not very sensitive toward moisture content.

To determine the influence of the inert atmosphere on the coating quality, several plating experiments were carried out in an argon-filled glove box. Results up to now show significant changes in coating quality and morphology in the case of lithium-based electrolyte baths and no significant changes in the case of non-lithium salt baths.

Using the electrochemical deposition cell described above, good quality adherent coatings of

Mo_2C were obtained under the following conditions:

electrolyte	Na_2WO_4	38 - 44 wt%
	K_2WO_4	40 - 46 wt%
	Na_2MoO_4	5 - 10 wt%
	Na_2CO_3	3 - 8 wt%
	$Na_2B_4O_7$	0.5 - 3 wt%
temperature	950 - 1000 °C	
cathode substrate	low-carbon steel	
anode	carbon, molybdenum	
cathodic current density	30 - 80 $mA.cm^{-2}$	

2. Operating parameters.

More detailed research was carried out using the above fixed electrolyte bath composition to determine the correlation of deposit quality with other process parameters such as temperature, anode material, cathode substrate, current modulation, etc.

The working temperature was varied from 900 to 1000 °C (below 850 °C no deposit was observed). Non-lithium electrolytes in all cases required higher working temperatures. Moreover, the additions of borate require even higher temperatures by 50 - 80 °C. Increase of temperature causes significant changes. Larger grain sizes are found at higher temperatures.

Both constant current and reverse and/or pulse current patterns were applied during plating. The latter produces smaller-grain-size coatings than the former, at the same working temperature. Reverse/pulse-current plating also makes higher current densities possible and appeared to be most effective in generating good quality coatings.

SEM examination of several coatings prepared at various plating conditions was carried out to establish the effect of plating conditions on the morphology, continuity and density of the carbide layer. A typical EDS spectrum for the good quality sample plated under condition described above is shown in Figure 2. As mentioned previously, our first experiments, which were done

without electrolyte purification, give us in most cases unreproducible results for the same plating conditions.

More significant information about the coating quality was obtained from examination of a sample cross section. In general it indicates approximately uniform thickness over an irregular substrate profile and a virtually dense pore-free coating. It seems that the deposit consists of two zones: a) a region near the iron interface containing both iron and molybdenum, which is probably a molybdenum interlayer and/or Fe-Mo alloy formed by diffusion and b) a zone further out which constitutes the true carbide coating. The nickel interlayer samples shows a much sharper Ni-Mo diffusion zone compared with the same diffusion zone consisting of Fe-Mo in the samples without nickel interlayer.

CONCLUSIONS

Results thus far indicate that the coating morphology depends strongly on melt composition, temperature and moisture content. Application of initial pre-electrolysis significantly changes the composition and morphology of the coatings. Non-lithium electrolyte baths do not require extensive purification. Addition of $Na_2B_4O_7$ to the basic non-lithium bath composition was observed to cause marked improvements in morphology and quality. Significant changes appear to be caused also by variations of deposition temperature. Further experiments are in progress.

Task 2. Preparation of Mo and Mo_2C by Plasma Enhanced Chemical Vapor Deposition (PECVD)

INTRODUCTION

Plasma-enhanced chemical vapor deposition (PECVD) has found application as a new technique for preparing thin protective films at much lower temperatures than by thermally driven CVD. As new applications, molybdenum or molybdenum carbide films have exploited the unique

properties of plasma-enhanced CVD films deposited at relatively low temperature. Based on last year's work, an effort has been undertaken to deposit Mo and Mo_2C films on a substrate of 2.54 cm (1 in) by 3.81 cm (1.5) in area. Using an orthogonal factorial design, a series of experiments has been carried out to investigate the effect of the evaporation rate of $Mo(CO)_6$ as a precursor. In these experiments, in order to generate a thicker film, the concentration of $Mo(CO)_6$ in the gas phase was increased by directly introducing $Mo(CO)_6$ powder in the reaction chamber, rather than supplying $Mo(CO)_6$ as a gas from a saturator reservoir. To estimate the approximate deposition rate of Mo or Mo_2C and the evaporation rate of $Mo(CO)_6$, the substrate and the molybdenum carbonyl powder were weighed (precision 10^{-4} g) before and after the discharge process.

EXPERIMENTAL

1. Electrode Preparation

To generate a reproducible surface condition and make quantitative analysis for Mo and C possible, a standard procedure for preliminary cleaning and weighing was adopted, as follows:

a) Clean the substrate surface with acetone solution and water, using an ultra-sonic treatment, followed by rinsing in alcohol and drying in air;

b) Weigh the cleaned substrate and the molybdenum carbonyl powder on a balance (precision 10^{-4} g);

c) Introduce the molybdenum carbonyl powder and the substrate into the reaction chamber;

d) After the experiment, weigh the substrate and deposit, and the remaining molybdenum carbonyl powder.

2. Conditions and Characterization Techniques

The following experimental parameters were varied: pressure (P), temperature (T), RF power, time (t), and gas flow rate (F). To limit the number of experiments, a statistical design based on the orthogonal table for 5 variables at 2 levels was used in Table 3. The actual parameters and

the results of the experiments are shown in Table 4. Two basically different conditions emerge from Table 4: vacuum evaporation, i.e., zero flow rate (level 1); and forced convection (level 2). The effects of these conditions are discussed below.

To compare and identify the compounds obtained by these experiments, EDXS of standard pure Mo_2C as a reference sample was carried out (see Figure 3). The composition of sample No.1 is identified as Mo_2C by EDXS (see Figure 4). Its morphology is shown in Figure 5 and Figure 6. The dark background is an apparently amorphous film, on which crystallites are growing. There are clearly two types of growth, as shown in Figure 5 and Figure 6. Further experiments and analysis are in progress.

RESULTS AND DISCUSSION

1. Optimal conditions

Initial conclusions have been drawn from the weight gain of the substrate about the optimal conditions to maximum evaporation rate, deposition rate and thickness. The results corresponding to Table 4 are shown in Figure 7. The analysis shows clearly that the factor which affects the deposition rate most is the flow rate of argon gas. This is understandable since the deposition rate may be increased strongly if introducing argon carrier gas into the reaction chamber can be avoided, because the argon gas dilutes the concentration of $Mo(CO)_6$ and decreases the deposition rate. The above results indicate that it is possible to depend on direct evaporation of $Mo(CO)_6$, i.e; $Mo(CO)_6$ is used as a discharge medium instead of using argon gas.

The second factor is the pressure in the reaction chamber. The lower the pressure, the higher the deposition rate, because the lower pressure promotes the evaporation of $Mo(CO)_6$ and makes the concentration of molybdenum carbonyl in the chamber increase. A third factor is the temperature and power density in the chamber. If the temperature and power density increase, the concentrations of radicals and gaseous ions also increase. This should accelerate deposition by increasing the evaporation rate. The deposition time is not an important factor; deposit

thickness would be expected to increase with time. Further experiments and analysis are in progress.

To analyze the deposition rate and thickness distribution of Mo and Mo_2C over a wide range of conditions, it is necessary to combine the $Mo(CO)_6$ reaction kinetics with a transport and reaction kinetic model of a parallel-plate PECVD reactor. This is done in Appendix 1. Analysis of the composition and microscopic morphology examination of the film morphology were carried out by EDXS. In general, the films were smooth, and their thicknesses were slightly larger than calculated from the weight gain assuming pure molybdenum. It is inferred that the film thickness is about 10 micrometers. Film morphology and the film properties were difficult to evaluate.

2. Reaction mechanism and modeling

As mentioned above, it is desirable to develop a two-dimensional transport and reaction kinetics model of a parallel-plate PECVD reactor to analyze the deposition rate and thickness distribution of Mo, C and Mo_2C deposition over a wide range of conditions. For such a model it may be necessary to adopt a reaction mechanism. The reaction mechanism of PECVD of molybdenum and molybdenum carbide is probably quite complicated. In Appendix 1, a simplified reaction mechanism is proposed and the outline of a 2-D model is given.

CONCLUSIONS

The PECVD procedure has been improved to minimize losses of $Mo(CO)_6$ in transport to the reaction chamber. The optimization of parameters points to low pressure, high temperature, high power density in the reaction chamber, and absence of argon gas flow in as favorable conditions. Thicker coatings, of up to a few μm thickness, have been obtained which show two different types of crystallites growing on an initially amorphous film.

REFERENCES

1. The Sodium Sulfur Battery, (eds. J.L.Sudworth and A.R.Tilley), Chapman and Hall, London, New York (1985) 141.

2. J. E. Battles and A. P. Brown, Proc. DOE/EPRI Beta Battery Workshop VI, Snowbird, Utah, USA, May 19-23 (1985) 7-1.

3. A. P. Brown and J. E. Battles, Ext.Abstr., 86-2, The Electrochem.Soc., Pennington, NJ (1986) 123.

4. A. P. Brown, J. Electrochem. Soc., 134 (1987) 1921.

5. B. Hartman, J. Power Sources, 3 (1978) 227.

6. S. A. Weiner, Report Ford Sodium/Sulfur Battery Program, National Science Foundation, Washington DC, (1975).

7. S. P. Mitoff, EPRI Report EM-683 (1975).

8. J. L. Sudworth, Chap.6 in "Electrochem. Power Sources. Primary and Secondary Batteries", (ed. M. Barak), IEE London (1980).

9. J. E. Battles et al., in "Corrosion Problems in Energy Conversion and Generation", (ed. C.S. Tedmon), The Electrochemical Soc., Corrosion Division, Princeton, NJ (1974).

10. G. Weiss, Ann. Chim., 1, 446, France (1946); J. Andrieux and G. Weiss, Bull. Soc. Chim. 598, France (1948).

11. H. T. Heinen, C. L. Barber and D. H. Baker, U.S. Bur. Mines, Rep. Invest., 6590 (1965).

12. A.K. Suri, A.K. Mukhjee and C.K. Gupta, J. Electrochem. Soc., 120 (1973) 622.

13. K. H. Stern, U.S. Patent 4 430 170 (1984).

14. D. C. Topor and J. R. Selman, J. Electrochem. Soc., 135 (1988) 384.

15. V.I. Shapoval, Kh.B. Khushkov and I.A. Novoselova, Ukr. Khim. Zh., 48 (1982) 738.

16. V.I. Shapoval, Kh.B. Khushkov, V.V. Malyshev, P.V. Nazarenko and N. P. Baidan, Zashch. Met., 22 (1986) 564.

17. V.A. Polishchuk, Kh.B. Khushkov and V.I. Shapoval, Electrokhim., 26 (1990) 305.

18. V.I. Shapoval, Kh.B. Khushkov, V.V. Malishev, V.T. Vesna and V.P. Maslov, Poroshk. Metall. (Kiev), 7 (1987) 43.

19. B. Aladjov, P. Yankulov, P. Angelov, K. Khushkov and G. Staikov, Proc. DOE/EPRI Beta Battery Workshop VIII, Chester, U.K., June 11-13 (1990) 29-1.

20. J. R. Selman and D. C. Topor, "Corrosion Resistant Coatings for High-Temperature High-Sulfur Activity Applications", Project 4549910 Annual Report, 1989.

21. Demetre J. Economon and Sang-Kyu Park, Proc. Eighth Symposium on Plasma Processing, (ed. G.S. Mathad and D.W. Hess), The Electrochem. Soc. Inc., Pennington, NJ 90-14 (1990) 185.

22. Demetre J. Economon, Sang-Kyu Park, and Gary D. Williams, Proc. Seventh Symposium on Plasma Processing, (ed. G.S. Mathad, G.C. Schwartz, and D.W. Hess), The Electrochem. Soc. Inc., Pennington, NJ 88-22 (1988) 17.

APPENDIX

Reaction Mechanism and Model Discussion:

The reaction mechanism of PECVD, of molybdenum and molybdenum carbide deposition is probably quite complicated. It is necessary to consider electron and ion transfer steps involving Mo, C, and O in the plasma state. The possible net reactions are only a few:

$$Mo(CO)_6 = Mo + 6CO \quad (R1)$$
$$2CO = C + CO_2 \quad (R2)$$
$$Mo(active) + C(active) = Mo_2C \quad (R3)$$

Under various reaction conditions in the chamber, only three final solid products are possible: Mo, Mo_2C and/or carbon.

Recently, there has been much interest in developing models of the plasma deposition process(21,22). In developing such models, there are a number of important phenomena which must be considered. These include the glow discharge chemistry, the electron density and energy distributions, ion transport in the reaction chamber, heat and mass transfer, and heterogeneous reaction kinetics. Even if the reaction kinetics were completely known, the present state of research does not allow one to include in a detailed way all the above phenomena in a model. Therefore, one focuses on specific aspects of the over-all process. Generally speaking, plasma models emphasize either the discharge chemistry, or the transport and reaction phenomena including relatively detailed chemical kinetics.

To analyze the process taking place under the conditions reported earlier, a transport and reaction model of a single-substrate, parallel-plate plasma reactor was outlined. The argon-$Mo(CO)_6$ plasma was chosen as a model experiment system. Feed gas enters uniformly and contacts the electrodes(Fig.8). Unreacted feed gas is pumped outward. The substrate is assumed to be in good thermal and electrical contact with the grounded lower electrode. In the ideal case, the substrate surface temperature is assumed constant ($T_{substrate} = T_{gas}$). Gas temperature variations in the chamber are also neglected because the solid molybdenum carbonyl, serving as the precursor, is contained in the saturator reservoir and its sublimation pressure is controlled by regulating the reservoir temperature. If the temperature is assumed constant, the sublimation

pressure should be constant in the reaction chamber. Generally, the temperature is below 300°C in PECVD systems. In this case, with $Mo(CO)_6$ as a precursor, 50-100°C is the working range.

The primary focus of this modeling effort is the concentration distribution of the deposited species and its effect on deposit uniformity. In particular, due to consumption of the depositing species on the substrate surface, large streamwise concentration gradients may develop at the substrate interface. Since the deposition rate is probably a function of the local deposition concentration as well as temperature, the resulting deposit is nonuniform. Transport and reaction kinetics theory can be used to analyze the reactant concentration distribution.

I) Flow Distribution:

The gas velocity distribution satisfies the Navier-Stokes equation and the continuity equation for parallel-plate geometry (Fig.9)

$$u\frac{\partial u}{\partial r}+w\frac{\partial u}{\partial z}=-\frac{1}{\rho}\frac{\partial p}{\partial r}+\nu\left[\frac{\partial^2 u}{\partial r^2}+\frac{\partial^2 u}{\partial z^2}\right] \tag{1}$$

$$u\frac{\partial w}{\partial r}+w\frac{\partial w}{\partial z}=-\frac{1}{\rho}\frac{\partial p}{\partial z}+\nu\left[\frac{\partial^2 w}{\partial r^2}+\frac{\partial^2 w}{\partial z^2}\right] \tag{2}$$

$$\frac{\partial u}{\partial r}+\frac{\partial w}{\partial z}=0 \tag{3}$$

The boundary conditions are

$$u=0 \text{ at } z=\pm L \text{ for all } r \tag{4}$$

$$w=0 \text{ at } z=\pm L \text{ for all } r \tag{5}$$

II) Transport and Reaction Kinetics:

The model is applied to $Mo(CO)_6$ gas which upon dissociation in the plasma produces precursors of the depositing(reactant) species. Emphasis is placed on the operating regime of a typical reactor(~1 torr, 13.56 MHz). Under such conditions, the glow discharge is usually sustained by bulk ionization. Some modulation may occur in the electron energy distribution at 13.56

MHz which in turn will modulate the deposition rate by electron impact dissociation. Hence, a time-independent reactant species concentration should be established. The steady-state mass balance for such a species (here subscripted 1) is, in general:

$$u\frac{\partial C_1}{\partial r}+w\frac{\partial C_1}{\partial z}=D_1[\frac{\partial^2 C_1}{\partial r^2}+\frac{\partial^2 C_1}{\partial z^2}]+\sum_i R_{i,1} \tag{6}$$

The second term on the right hand side of Eq.6 represents the consumption of reactant species by electron impact dissociation of molecules and a series of chemical reactions. Surface reaction kinetics of Mo and C deposition enter into the boundary conditions and must be considered. Therefore, one may need to make use of the Boltzmann equation for the reactant species concentration and the Poisson equation for the species potential distribution. It is expected that the model will help determine realistic ranges for the reaction kinetic parameters.

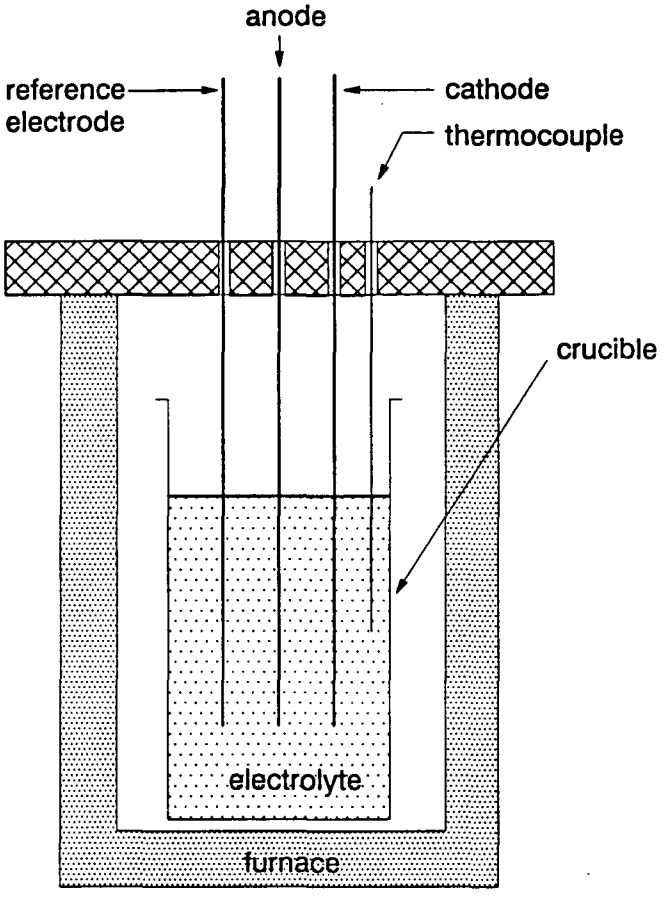

Figure 1. Plating Cell Assembly

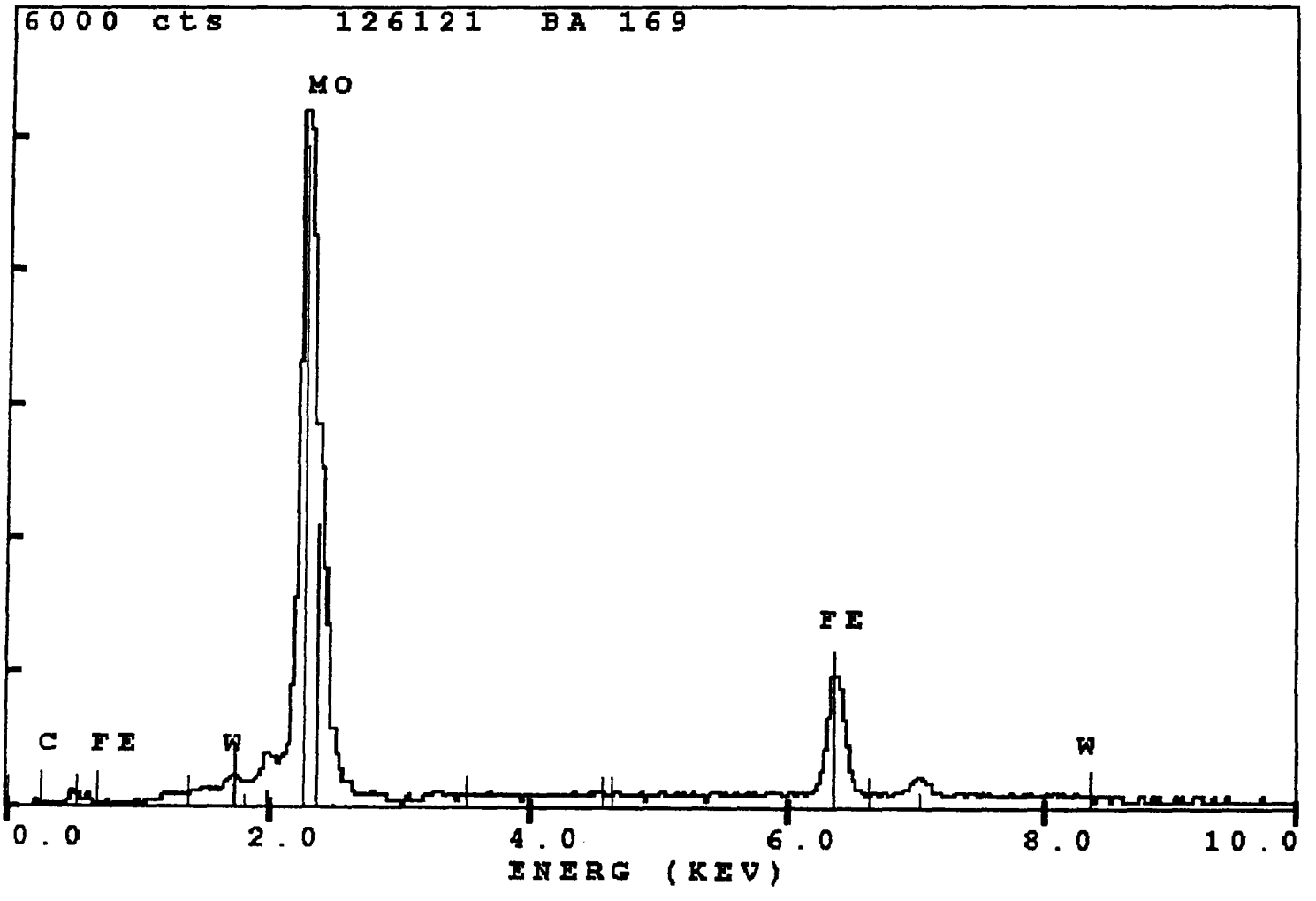

Figure.2 EDXS spectrum of a deposit obtained by MSECD

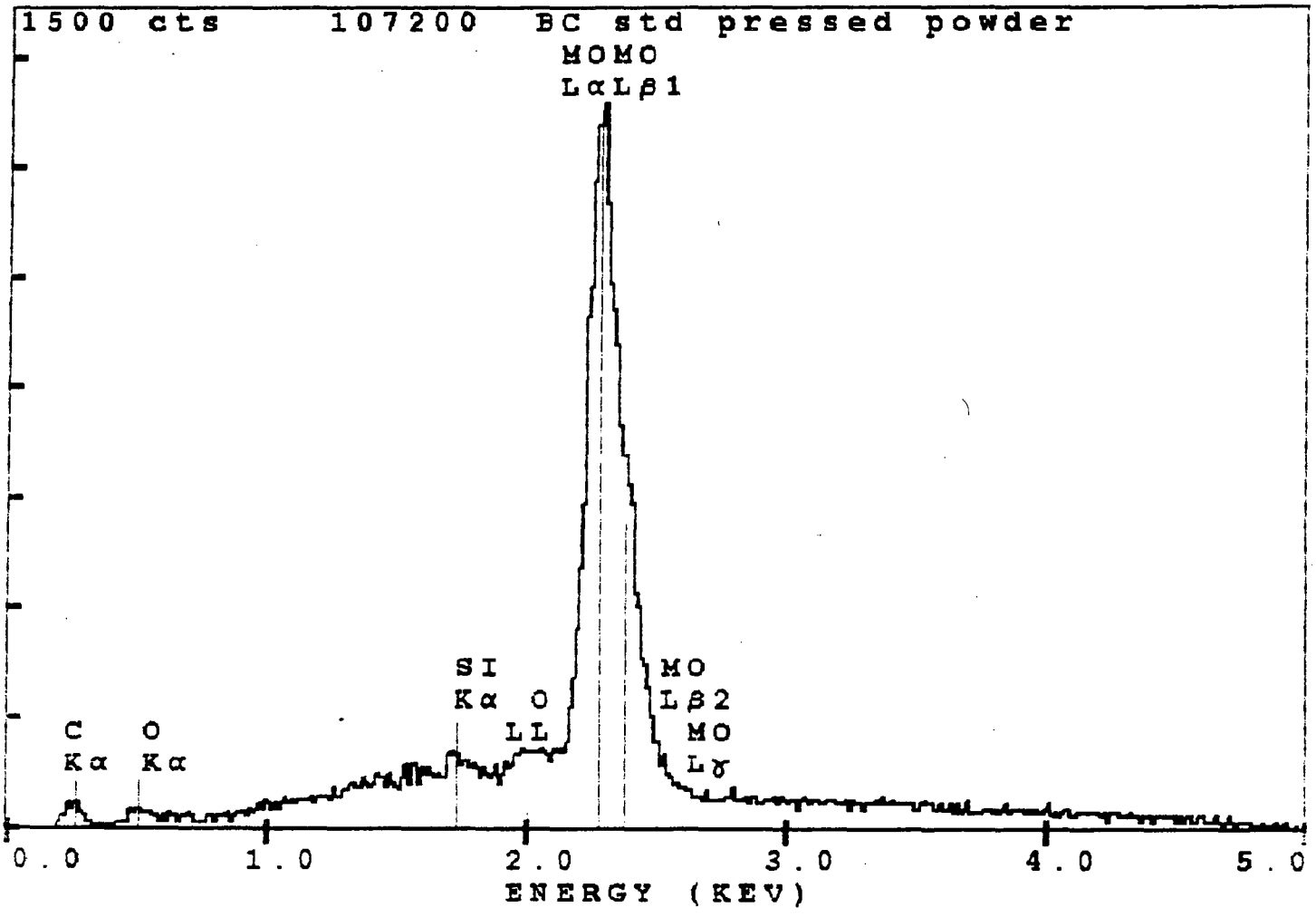

Figure.3 EDXS spectrum of Mo_2C standard (pressed powder)

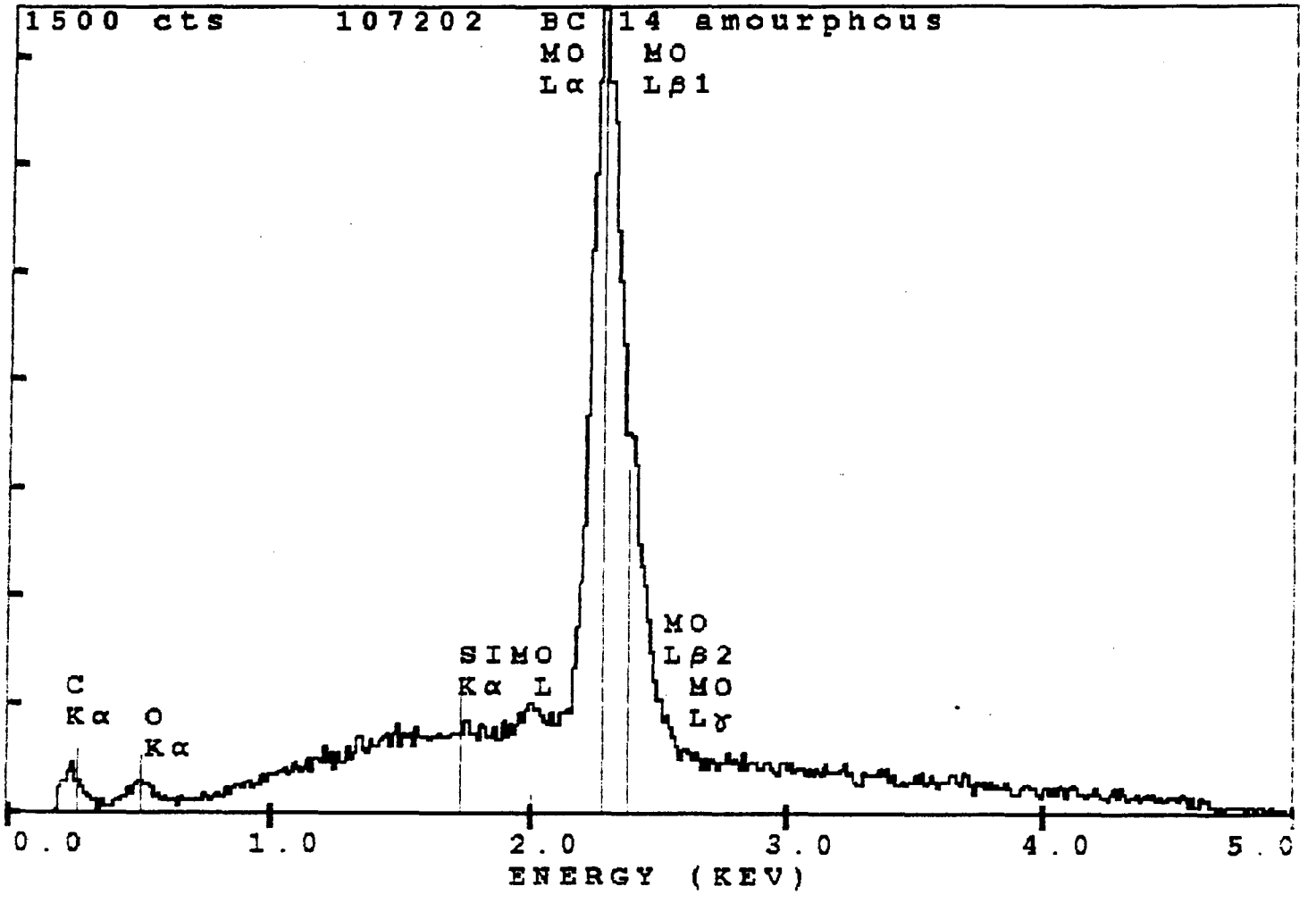

Figure.4 EDXS spectrum of deposit by PECVD on glass

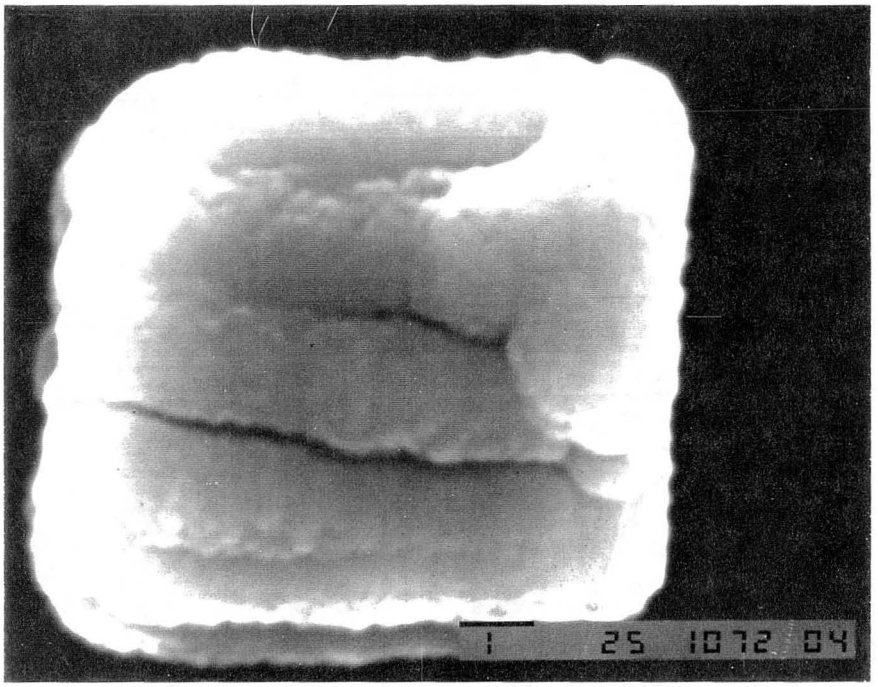

Figure.5 SEM photograph of crystallites on amorphous film deposited by PECVD; first type

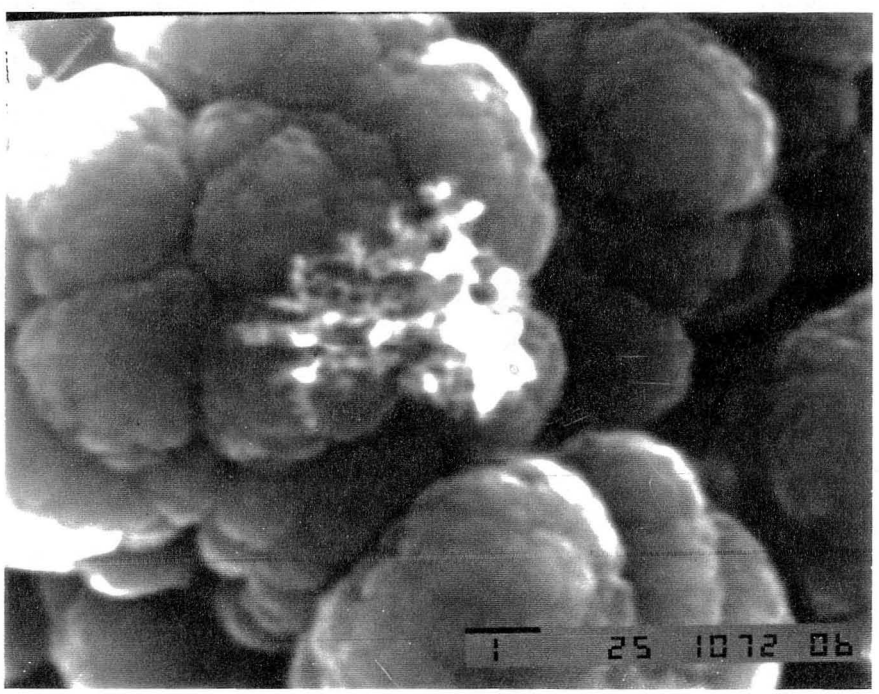

Figure.6 SEM photograph of crystallites on amorphous film deposited by PECVD; second type

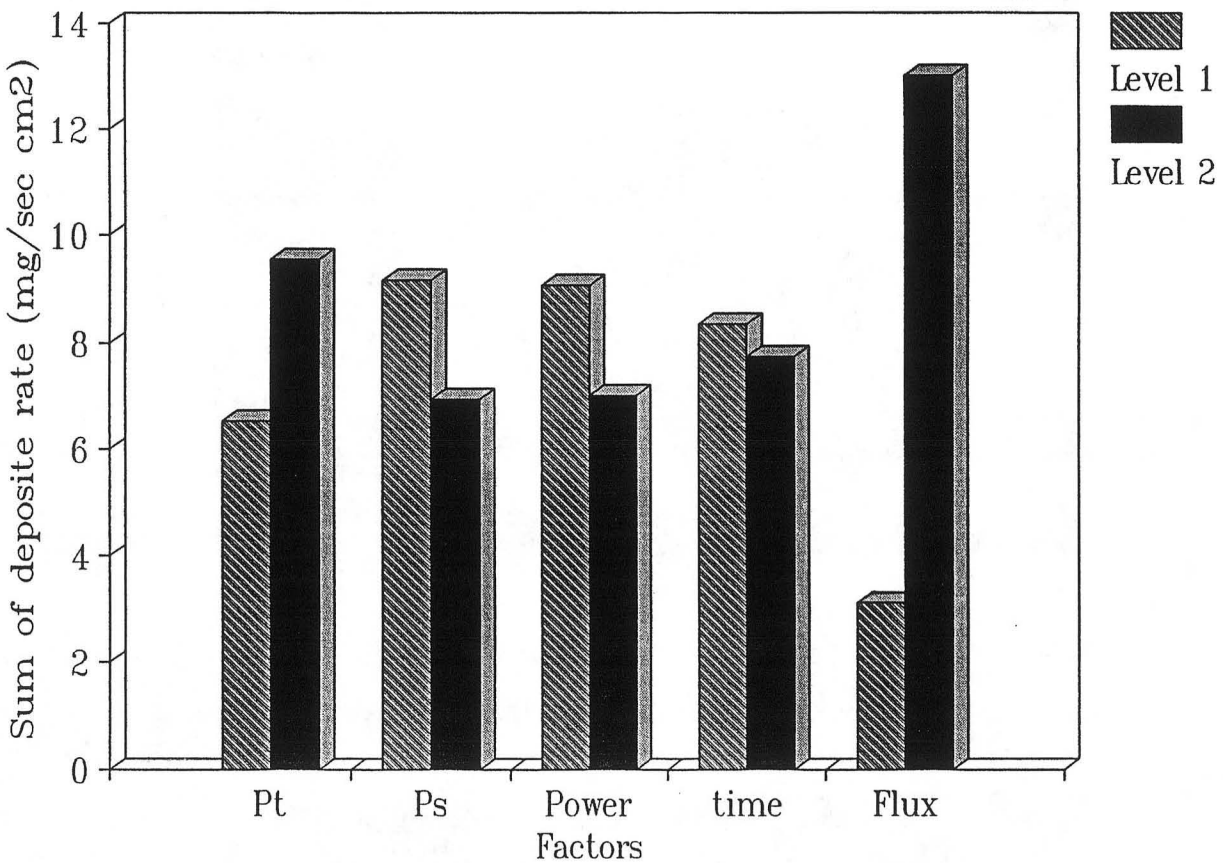

Figure.7 Factorial Effects on the deposition rate in PECVD

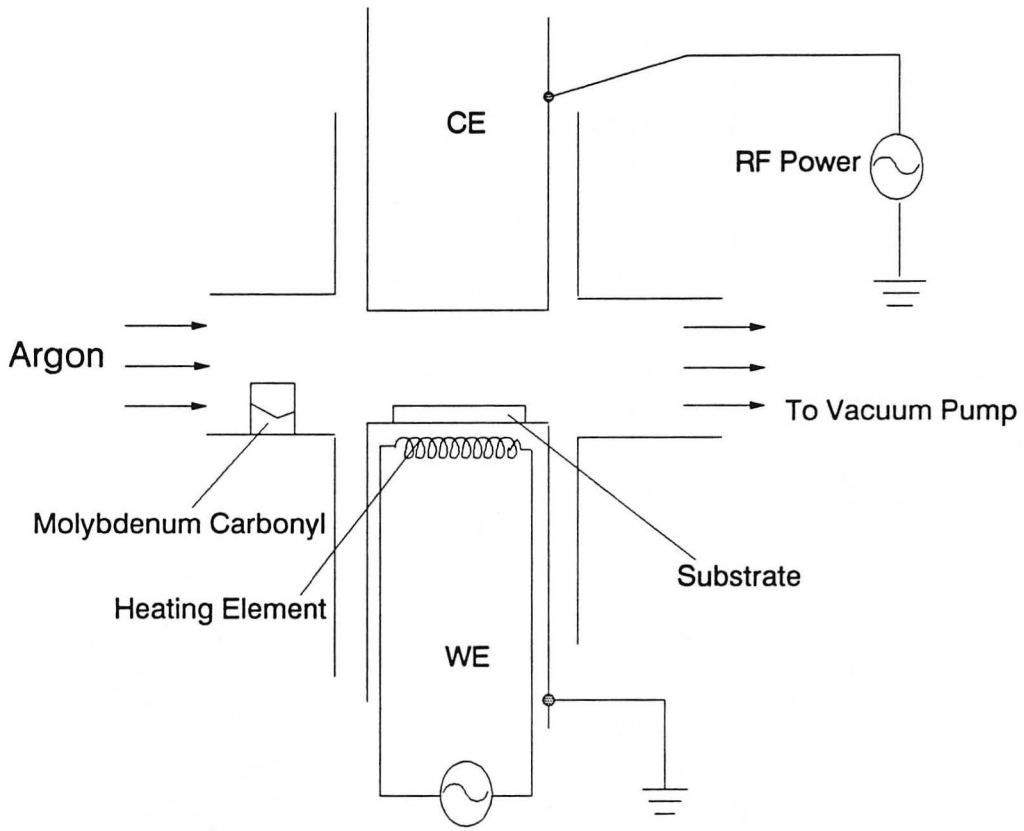

Fig.8 The configuration of the reaction chamber

CE-Counter Electrode WE-Working Electrode

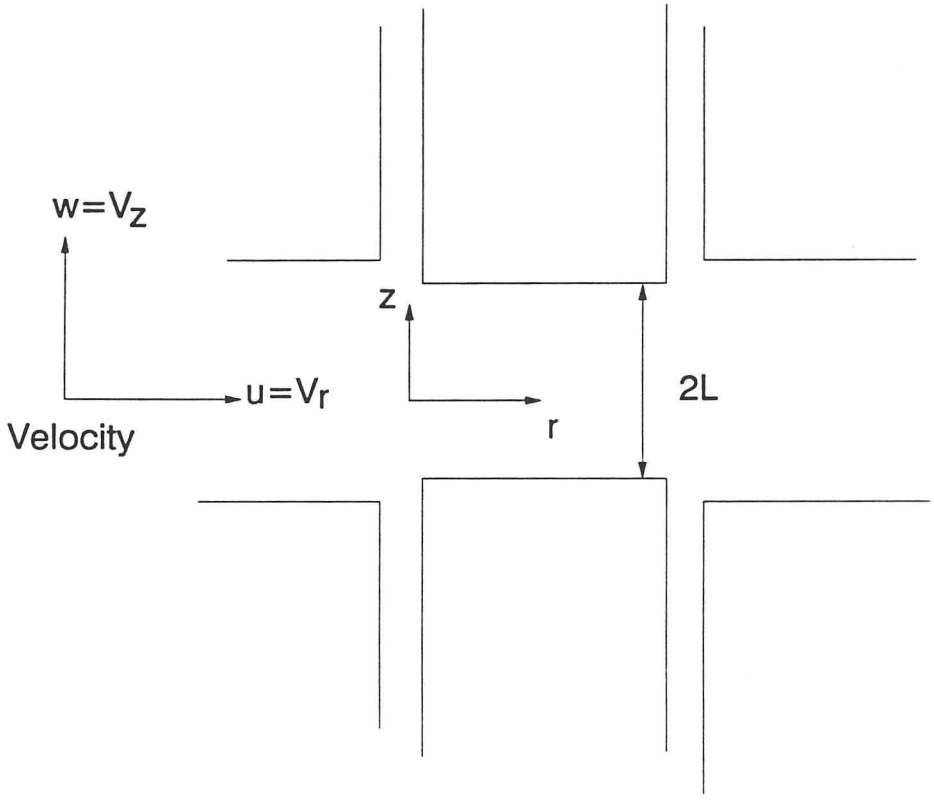

Fig.9 Parallel-plate geometry of the PECVD cell

Table 1. Conditions for MSECD from Fluoride and Oxide Baths.

Conditions	Fluoride-based electrolyte, wt%	Oxide-based electrolyte wt%
Electrolyte composition	LiF-NaF-KF (FLINAK) 29-11-60 Li_2MoO_4 5-10 K_2CO_3 10-20	Na_2WO_4 38-44 K_2WO_4 40-46 Alkali molybdate 5-10 Alkali carbonate 3-8 Alkali borate 0.5-3
Temperature	800 - 850 °C	900 - 1000 °C
Atmosphere	Prepurified Argon with: Oxygen 50 - 100 ppm Water 5 - 10 ppm	Air
Current density	50 - 100 $mA.cm^{-2}$	25 - 50 $mA.cm^{-2}$
Thickness	20 - 50 μm	10 - 30 μm
Substrate	Low-Carbon Steel with Ni interlayer	Low-Carbon Steel

Table 2. Chemical Composition of the Electrolyte Baths Used in the Plating Experiments.

Bath # Chem.Comp.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Na_2WO_4	●	●	●	●	●	●	●	●	●	●	●	●	●	●
K_2WO_4	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Li_2MoO_4	●	●	●											●
Na_2MoO_4				●	●	●					●			
K_2MoO_4							●	●	●			●		
MoO_3										●			●	
Li_2CO_3	●			●			●			●				●
Na_2CO_3		●			●			●			●		●	
K_2CO_3			●			●			●			●		
$Na_2B_4O_7$											●	●	●	●

Table.3 Design parameters for a 5-variable 2-level test design

Factors	P	T	Power	t	Flux
Level 1	2	50	40	40	100
Level 2	0.5	25	20	20	0
Unit	(torr)	(°C)	(Watt)	(min)	(sccm)
1	2	50	40	20	0
2	0.5	50	20	20	100
3	2	25	20	20	0
4	0.5	25	40	20	100
5	2	50	20	40	100
6	0.5	50	40	40	0
7	2	25	40	40	100
8	0.5	25	20	40	0

Standard Orthogonal Table

Col No.	1	2	3	4	5	6	7
Ex No.							
1	1	1	1	2	2	1	2
2	2	1	2	2	1	1	1
3	1	2	2	2	2	2	1
4	2	2	1	2	1	2	2
5	1	1	2	1	1	2	2
6	2	1	1	1	2	2	1
7	1	2	1	1	1	1	1
8	2	2	2	1	2	1	2

Table 4

Factors affecting the deposition process

Factors	P_t	P_s	Power	time	Flux	R_{evp}	$R_{dep}x10^4$
Unit	torr	torr	w/cm^2	min	cc/min	mg/sec	mg/scm^2
Level 1	2	1.24	1	40	100		
Level 2	0.5	0.14	0.5	20	0		
1 (s-14)	2	1-3	1	20	0	0.303	3.273
2 (s-18)	1	1	0.5	20	50	0.181	1.033
3 (s-12)	2	0.1	0.5	20	0	0.123	2.325
4 (s-15)	1	0.2	1	20	70	0.193	1.12
5 (s-16)	2	1	0.5	40	100	0.127	0.56
6 (s-13)	0.5	5	1	40	0	0.336	4.307
7 (s-17)	2	0.2	1	40	100	0.084	0.388
8 (s-11)	0.4	0.13	0.5	40	0	0.168	3.1
Sum 1	6.546	9.173	9.088	8.355	3.101		16.106
Sum 2	9.56	6.933	7.018	7.751	13.005		
$\|S_1-S_2\|$	3.014	2.24	2.07	0.604	9.904		
	S1<S2	S1>S2	S1>S2	S1=S2	S1<S2		
	level 2 low Pt	level 1 high Ps	level 1 h power		level 2 w/o flux		

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