Review

A Review of Laser Enhanced Plating and Etching for Electronic Materials

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レーザー加速めっきおよびエッチングに関する理論と応用について、特にマイクロエレクトロニクス材料への応用について解説を行う。ニッケル、金、銅電析に関して金属化した基板上にフォトマスクを使わずアルゴンレーザーを利用してめっきする方法について概説する。0.5 mm スポットの金メッキではレーザーを用いるとベリリウム銅基板上で通常の金めっきの場合の数 10 倍の速度である 10 $\mu\text{m/s}$ にまで析出速度を上げることが可能である。スチール、シリコンおよびセラミックスのエッチングについてのレーザー加速エッチングについても解説する。

1 Introduction

Laser enhanced plating and etching have become increasingly interesting in recent years as a method of rapid maskless patterning. Such patterning is particularly useful in the microelectronics industry where applications to circuit design and circuit repair are most often cited. The ability to focus the laser to dimensions on the order of an optical wavelength in combination with the highly non-linear plating/etching enhancement rates as a function of laser power in the region exposed to the focused radiation makes it possible to access and pattern micron sized regions with minimal background effects. This localization feature produces patterning without the use of masks. The present discussion will describe plating/etching processes that are primarily photothermal and will not describe the many photochemical processes that can also be utilized for maskless patterning.

2 Laser Enhanced Plating : Early Experiments

The experimental arrangement that was first used to demonstrate laser enhanced plating is shown in Fig. 1 and in conjunction with a

NiCl_2 solution. The following results were obtained: 1) Localized plating in the region of absorbed laser radiation at rates up to 10^3 times faster than background rates^{1,2)}, 2) the ability to deposit Ni on substrates normally difficult or nearly impossible to electroplate by conventional means, 3) the etching of holes in stainless steel on the order of 50–100 μm in

Fig. 1 Plating cell showing laser beam directed through the transparent sample to be incident on the glass-metallized predeposited film interface¹⁾. Shown also are scanning mirror, chopper and laser. An additional mirror, not shown, can be interposed to bring the laser to the electrolyte-metal surface, *i.e.*, front illumination. A dropping resistor is used to measure current flow, in particular, current with and without laser illumination.

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diameter, 4) the thermal nature of the plating/etching mechanism. This was verified by directing laser light to the metallized substrate surface from two directions, from the solution to the metal and from the optically transparent substrate side to the absorbing metal using the apparatus of Fig. 1 with an additional adjustable mirror not shown. For laser illumination through the transparent glass substrate, no photons reach the electrolyte due to the 2–3000 Å thick premetallization. However, the depositions from both front and interfacial laser irradiation were found to be essentially the same in diameter and thickness. Hence photons cannot play an important role as excitation sources of the interface, while heat generated by photon absorption is equivalent for the two experiments. By using two substrates of widely differing thermal conductivity, i.e., thin films deposited on glass and on single crystal sapphire, it was found that the latter gives rise to thinner depositions covering however a larger area than that obtained with the glass substrates. These results are consistent with pyrolytic mechanisms with the higher conductivity material giving rise to less heat localization and hence a wider but thinner depositon.

A more detailed investigation of the plating mechanisms was subsequently undertaken utilizing a three electrode potentiostat to study the Cu/Cu^{2+} system³⁾. For these experiments, a special electrode was constructed having a diameter on the order of that of the focused laser beam at the point of incidence on the cathode. This was achieved using a metallized glass substrate covered entirely, except for a small hole, with a photoresist layer acting as an insulator, Fig. 2. To study the laser plating enhancement as a function of overpotential,

Fig. 2 Structure of a metallized-glass cathode using photoresist to produce a small electroactive area, approximately equal in size to the focused laser beam diameter³⁾.

Fig. 3a Polarization curve for copper electro-deposition (current and overvoltage are negative); electrode diameter, 550 μm [Ref. 3].

Fig. 3b Polarization curve for the electrode with 200 μm diameter active area. Laser power, 210 mW ($6.7 \times 10^2 \text{ W/cm}^2$). Laser is applied at 50 mV intervals causing large current spikes³⁾.

polarization curves were taken both with and without the laser directed through the hole onto the small cathode. Fig. 3a shows the current dependence on overvoltage without the laser, while Fig. 3b gives the dependence with periodic laser radiation ($6.7 \times 10^2 \text{ W/cm}^2$ argon ion laser) applied at 50 mV intervals. The temperature at the interface is estimated to be $\sim 120^\circ\text{C}$ in the steady state for this incident flux. A comparison of the curve of b) with and without the laser gives a direct measure of the plating enhancement afforded by the laser by the laser assuming comparable plating efficiencies. It is evident that a larger enhancement occurs at the larger overpotential up to the point of hydrogen evolution. The fact that a finite current flows at zero overpotential is due to a shift in the equilibrium (rest) potential to more positive values with in-

creasing temperature. Thus, at zero overpotential the enhancement factor, i.e., ratio of plating current with and without the laser, approaches infinity.

The results of experiments utilizing these small cathodes have helped to elucidate the following principal laser plating mechanisms³⁻⁵:

1) At low overpotentials where plating is kinetically controlled, a local increase in temperature increases the charge transfer rates and hence the plating current. The plating current density is given at low overpotentials by the Butler-Volmer equation:

$$i = i_0 \left[\exp(1 - \beta) \frac{\eta F}{RT} - \exp\left(-\beta \frac{\eta F}{RT}\right) \right] \quad (1)$$

where β is an exchange coefficient, η the overpotential, i_0 the exchange current density, R the gas constant, and T the absolute temperature. The exchange current density is given by

$$i_0 = nF \frac{kT}{h} C_A \exp[-(\Delta G_C + \beta F \Delta \phi_e)/RT] \quad (2)$$

where n is the number of charges per atom undergoing reduction, F , Faraday's constant, ΔG_C the chemical free energy of activation, C_A the ion concentration/cm³, h , Planck's constant, k , Boltmann's constant, and $\Delta \phi_e$ the equilibrium potential. The temperature dependence of i_0 is dominated by an Arrhenius term, $\exp(-\Delta G_C/RT)$. Therefore, the kinetics of the reaction always increase with increasing temperature, irrespective of $\Delta \phi_e$ (since ΔG_C is positive and greater in absolute magnitude than $\Delta \phi_e$). 2) A shift in the rest potential, $\Delta \phi_e$ to a more positive value occurs for the system Cu/Cu²⁺ with increasing temperature. This positive shift takes place with certain electrolytes including the gold/gold cyanide interface. The temperature dependence of $\Delta \phi_e$ has the effect of shifting the entire overpotential curve to the left (Fig. 3b) in the region of the cathode undergoing laser heating giving rise to a higher current for a fixed overpotential. The temperature dependence of $\Delta \phi_e$ is obtained from the negative entropy change of the system where

$$\frac{d\Delta \phi_e}{dT} \propto \frac{\partial \Delta G_C}{\partial T} = -\Delta S^\circ \quad (3)$$

with S° the entropy. In general, this can give a positive or negative value, for $d\Delta \phi_e/dT$ and has been found to be negative for NiSO₄, sodium citrate plating solution in contact with a Ni electrode³). 3) A large plating enhancement in the mass transport limited current region occurs due to the local microstirring of the fluid driven by the large thermal gradients produced by local laser absorption at the cathode. Additional stirring can also occur as a result of nucleate boiling. The fluid agitation brought about by local stirring and boiling causes a resupply of ions to the otherwise depleted region. The limiting current density, i_l ,

$$i_l = \frac{nFDC}{\delta} \quad (4)$$

is thereby increased by virtue of the decrease in the diffusion length, δ . Here, D is the diffusion constant which is also temperature dependent, increasing with increased temperature and C the molar concentration far from the cathode (bulk concentration).

3 Other Types of Laser Enhanced Plating

The nature of the enhancement mechanisms as outlined in the previous section gives rise to two additional types of laser enhanced plating which utilize no external driving force (EMF source). These electroless plating effects have both been experimentally verified in earlier reports³⁻⁵). In laser enhanced electroless plating, relatively fast plating rates occur in the region of laser absorption while virtually no background plating takes place elsewhere. Charge balance is maintained via a catalytic reducing agent incorporated in the solution. Experiments with electroless nickel deposits resulted in rates of $\sim 1000 \text{ \AA/s}$ on metallized glass and activated glass substrates using 2-3 W of focused argon laser light. Thermobattery or laser enhanced exchange plating occurs when there is a shift in the rest potential to a more positive value with increasing temperature³⁻⁵). As the region absorbing laser light increases in temperature relative to the rest of the substrate, the local shift in rest potential causes increased plating in the hotter region with simultaneous etching

in the cooler peripheral regions. The simultaneous plating and etching maintains charge conservation and overall charge neutrality. For a glass substrate with a metallized coating undergoing this form of deposition, the plating process continues at the center until the peripheral region is etched away, producing electrical isolation of the center region. For those electrolytes possessing a negative temperature shift in rest potential, dissolution (etching) occurs in the center with a simultaneous peripheral build-up (plating) as observed for NiSO_4 in conjunction with a nickel coated substrate⁹). The thermobattery effect for gold depositions has been demonstrated extensively using a computer controlled table to move the cathode with respect to the laser to form a variety of patterns⁹).

4 Recent Results : Gold Depositions

Recent interest in laser enhanced plating has centered on high speed deposition of gold⁶⁻⁹). This metal is of particular interest to the microelectronics industry where large quantities of gold and other precious metals are required for electrical contact areas on circuit boards and pin connectors. With present deposition techniques, gold becomes deposited where it is not required, causing considerable waste of this precious metal. The substrate material commonly used for these macroelectronic connectors is nickel plated Be-Cu, which has proven difficult to mask, resulting in gold consumption far greater than necessary. A high speed localized plating can therefore save time, as well as precious metal and space costs. The space saving occurs from the use of smaller plating tanks, made possible by the reduced time that the part has to be in contact with the plating solution. This, in turn, makes it possible to maintain a smaller gold inventory, an additional cost saving. Work on laser enhanced gold depositions in the form of 0.5-1 mm diameter spots and 100 μm wide lines on nickel plated Be-Cu substrates has been previously reported⁷). These experiments utilized commercially available gold sulfite and gold cyanide plating solutions. It was found that laser enhanced electroplating rates as high as 1 $\mu\text{m/s}$ could be achieved using Autronex 55

GV (Selrex Corp., Nutley, NJ) without Co or Ni additives, resulting in soft gold deposits. These experiments used up to 20 W of argon laser power focused to spots of 0.5-1 mm diameter. Depositions were made under a variety of electrochemical and laser parameters. Examination of both cross sectioned deposits and SEM micrographs of the deposited surfaces was used to analyze their quality. Attempts to laser deposit at higher deposition rates resulted in dendritic and porous morphologies believed to occur due to plating at or above the limiting current density, Eq. 4. Under these high currents a poor morphology results due to the lack of a sufficient resupply of ions, *i.e.*, mass transport limitations. An example of a quality laser plated gold spot on Be-Cu is shown in Fig. 4. The smooth surface morphology is typical of very small grain size. The cross sectioned gold indicates a dense deposit, pore and void free. This spot was deposited at a rate of 1 $\mu\text{m/s}$ in contrast to a maximum rate of 0.1 $\mu\text{m/s}$ observed for a highly agitated solution utilizing otherwise standard plating technology¹⁰). Other attempts at laser enhanced plating of gold on metal substrates have used intermediate deposition of lower thermal conductivities to enhance the local temperature rise from the laser radiation¹¹).

A method to greatly increase the mass transport over and beyond that afforded by the laser microstirring has been recently developed yielding an order of magnitude increase in plating rates over the earliest reported rate for laser enhanced gold deposition¹²). A schematic of this technique, termed laser enhanced jet plating, is shown in Fig. 5. Here, a free standing jet of electrolyte emanating from a

Fig. 4 a) Surface of laser plated spot using Autronex 55 GV, pure gold. b) High magnification SEM, the deposit showing in detail the excellent surface morphology⁷).

Fig. 5 a) Diagram of free jet (no laser) showing fundamental regions of jet of radius r_0 , region I; II stagnation flow region with r and z dependence for velocity of jet and electric fields. Region III, wall jet, velocity and current varies mainly in the r direction and carries low current densities since wall jet is thin and hence much more resistive compared to stagnation region¹²⁾.

pressurized chamber through a nozzle impinges on the cathode. The anode, housed in the pressure chamber, consists of shim stock of gold or platinum with a hole sufficiently large to allow passage of the laser light prior to its passage through the nozzle. Anode-cathode current flow is limited to the region of the jet column. Deposition occurs mainly in the stagnation region (Fig. 5a) and to a much lesser degree extends radially into the wall jet region. The current density in the wall jet much smaller than in stagnation region so that plating rates are proportionately smaller. The jet stream in the laser-jet configuration also serves as a light guide for the beam directing the radiation to the cathode to form a laser enhanced jet plating system. Most of the light absorption occurs in the stagnation region at the cathode so that the peripheral plating is not laser enhanced. The cathode (substrate) in these experiments was mounted on an arm attached to the computerized precision table for patterning using the relative motion of the cathode with respect to the stationary nozzle and jet. A summary of hydrodynamic and laser parameters used for gold patterning experiments is presented in Table I. Figure 6 shows optical micro-

Fig. 6 Cross-sections of laser gold on nickel plated Be-Cu substrates, 200 μm thick; Plating current density, 11 A/cm². Top layer is electrodeposited nickel to protect gold during cross-sectioning and polishing. Laser-jet plating times and resulting thicknesses are : a) 0.5 s, 4.5 μm b) 1 s, 8 μm c) 5 s, 30 μm [Ref. 12].

Fig. 7 Cross-sections of jet plating, but without the laser, Substrates and current densities as in Fig. 6. a) 1 s, 3 μm b) 5 s, 12.5 μm c) 10 s, 25 μm. Note voids throughout gold deposit, deposit, independent of gold thickness¹²⁾.

Table 1 Gold plating solution and laser-jet cell parameters

Gold solution	Sel-Rex* Autronex 55 GV, Au cyanide, no additives, 4 Tr. Oz. Au/gal
Solution temperature	60 °C
Jet orifice	0.05 cm diameter, ~0.2 cm long
Linear flow velocity	1.0×10^3 cm/s
Reynolds number	5.5×10^3
Nozzle-cathode spacing	~0.5 cm
Plating current density	1–16 A/cm ²
cw Laser power into jet	~25 W maximum

* Sel-Rex, Div. of Oxy-Metal Industries Corp., Nutley, NJ 07110.

scope photographs of cross sectioned laser plated gold deposits on nickel plated Be-Cu substrates using parameters of Table 1. For comparison, Figure 7 shows cross-sectioned samples made identical conditions except without laser radiation. The important features of the laser jet samples are 1) plating rates up to $10 \mu\text{m/s}$ for incident power levels of 20 W, 2) void free dense deposits of excellent metallurgical quality, 3) good adhesion to the substrate. In contrast, the samples prepared with the jet and no laser power show void formation independent of film thickness. This indicates that at these high current densities, voids are initiated very near the nucleating surface and propagate into the film as it grows to larger thicknesses. Jet plated gold samples without voids could not be grown at rates faster than $1 \mu\text{m/s}$. We surmise that the laser radiation and the resulting local heat may be annealing the film during deposition while also enhancing nucleation sites on the sample substrate. The latter effect can be due in part to laser substrate cleaning of a thin oxide layer. The dissolution of this oxide occurs during the initial interval of laser absorption and consequent local heating.

For the high plating rates afforded by this method, it is possible to consider an automated reel to reel plating system for the manufacture of gold contacts on Be-Cu parts. For the 1–2 μm gold thicknesses generally required, a rate of $10 \mu\text{m/s}$ permits plating in 100–200 ms, or a throughput of up to 10 parts/s

for a single 20 W laser directed through a single nozzle. Both hard and soft gold can be plated by this method.

The laser jet electroplating technique has recently been applied to copper electrolytes for high speed maskless copper plating. Preliminary results indicate the main effect of the laser is to improve the surface morphology of the copper deposits. Plating rates, on the other hand, did not appreciably increase for molar concentrations of CuSO_4 in the range 0.2–1.0 M, a behavior quite different from that observed for gold. Further investigations of the Cu system using the laser jet arc continuing.

5 Laser Etching

By reversing the polarity of the cathode and anode of the experimental arrangement of Fig. 1, laser enhanced etching has been achieved^{1,2}. This etching technique has been used to produce $50 \mu\text{m}$ diameter holes in stainless steel stock (Fig. 8) using NiCl_2 solution as the electrolyte⁵. It is also possible to obtain high speed laser enhanced etching without the use of externally applied potentials. We have demonstrated enhanced chemical etching (machining) by patterning a variety of ceramics as well as single crystal silicon using an intense laser beam to locally melt the substrate¹³. In these experiments the high local temperatures caused intense stirring of the solution thereby allowing fresh ions to enter the region undergoing laser processing while simultaneously dispersing the reacted fluid. The local temperature increase also causes an increase in the chemical reactions which are thermally acti-

Fig. 8 $50 \mu\text{m}$ diameter hole electroetched in $50 \mu\text{m}$ thick stainless steel shim stock⁵. No post processing was used to obtain shape.

Fig. 9 Volume removal rate vs. laser power for alumina/TiC ceramic and (111) silicon (Curves drawn as aid to the eye)¹⁹⁾.

vated.

Etching rates in terms of volume removal for (111) Si processed in concentrated KOH are shown in Fig. 9 as a function of incident laser power. Under standard etch conditions, KOH will not etch this crystal orientation but will etch (100) Si strongly. In the present experiments, however, the intense heat produces local melting and consequently a loss of any crystal symmetry. Figure 9 also shows the rates for the etching of alumina/TiC, a ceramic used in a number of important microelectronic applications. The etch rates for this material are approximately an order of magnitude higher than Si for a fixed incident laser power. For Si, an average etch rate of 15 $\mu\text{m/s}$ has been observed in the laser etching of through holes in 10 mil wafers using a power density of 10^7W/cm^2 . Instantaneous etch rates in alumina/TiC ceramic of 200 $\mu\text{m/s}$ have been observed for an incident power density of 10^8W/cm^2 .

6 Conclusion

Experiments on laser enhanced plating and etching have demonstrated the ability to bring

about plating rates as high as 10 $\mu\text{m/s}$ which is 10^2 to 10^3 times as rapid as that obtainable with more conventional techniques, standard in the industry today. In certain cases, the laser enhanced technique also leads to an improvement in the quality of deposit. The pyrolytic effects caused by the laser absorption also cause localized cleaning of the substrate, thereby making it possible to obtain on substances normally hard or impossible to plate, good adhesion of the deposit to the substrate and enhanced nucleation on the surface. The ability to confine the light to micron sized dimensions leads to maskless patterning on a micron sized scale. High speed patterning of this type is becoming increasingly interesting for circuit design, circuit repair, and localized deposits on microelectronic connector parts. Localized etching also has numerous applications in the field of microelectronics.

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References :

- 1) R.J. von Gutfeld, E.E. Tynan, R.L. Melcher and S.E. Blum, *Appl. Phys. Lett.* **35**, 651 (1979).
- 2) R.J. von Gutfeld, E.E. Tynan and L.T. Romankiw Extended Abstract 472, p. 1185 Electrochem. Soc. Los Angeles, CA (Oct. 14-19, 1979).
- 3) J.-Cl. Puipe, R.E. Acosta and R.J. von Gutfeld, *J. Electrochem. Soc.* **128**, 2539 (1981).
- 4) R.J. von Gutfeld and J.-Cl. Puipe, *Oberfläche/ Surface* **22**, 294 (1981).
- 5) R.J. von Gutfeld, R.E. Acosta and L.T. Romankiw, *IBM J. of Research and Development* **26**, 136 (1982).
- 6) R.J. von Gutfeld and L.T. Romankiw, *Gold Bulletin* **15**, 120 (1982).
- 7) M.H. Gelchinski, L.T. Romankiw and R.J. von Gutfeld, Ext. Abstracts 82-2 p. 206, Electrochem. Soc., Detroit, MI (Oct. 1982).
- 8) R.J. von Gutfeld, M.H. Gelchinsk and L.T. Romankiw, SPIE Proc. on Conf. on Laser Processing of Semiconductor Devices **385**, 118 (1983).
- 9) L.T. Romankiw, R.E. Acosta, M.H. Gelchinski and R.J. von Gutfeld, Proc. of Symp. on Electroplating and Waste Recycle, New Develop. and Trends,

- Cleveland, Ohio, August 30, 1982, Electrochem. Soc., Electrodeposition Div. Vol. 83-12, p. 66.
- 10) D.R. Turner, *Thin Solid Films* **95**, 143 (1982).
- 11) H.K. Kuiken, F.E.P. Mikkers and P.E. Wierenga, *J. Electrochem. Soc.* **130**, 554 (1983).
- 12) R.J. von Gutfield, M.H. Gelchinski, L.T. Romankiw, and D.R. Vigliotti, *Appl. Phys. Lett.* **43**, 876 (1983).
- 13) R.J. von Gutfield and R.T. Hodgson, *Appl. Phys. Lett.* **40**, 352 (1982).

協会レポート

第 19 回腐食・防食セミナー報告

本委員会は昭和 28 年に岡本剛教授を初代委員長として発足し、本委員会が主体となって腐食防食討論会も生れ、腐食における電気化学の重要性が徐々に認識されるに至った。セミナーの No. は、次の委員長向坊隆教授の時(昭42)のそれが第1回とされ、以来向正夫教授→藤井晴一教授→田島栄教授と続き、活発なセミナーが開かれてきた。その主なるものとしては、核生成、白金電極、陽極酸化皮膜、高温酸化、電解加工、電池のアノード挙動、化学装置と材料、インヒビター、電気防食、分極測定、腐食系における酸素の挙動、皮膜で覆われた電極の化学、腐食教育、腐食試験法の進歩、金属の動態—不動態を利用した電気化学的興奮模型、Al³⁺ イオンの挙動と応用等が挙げられ、きわめて有意義な講演と討議がなされてきた。

今回はその第 19 回目で、下記セミナーが行なわれた。とき 5月15日(火)13:00—17.00, ところ 家の光会館

1. 溶融塩中における腐食の電気化学

溶融塩による金属の腐食を電気化学的現象として解析し、さらに実機における電気化学的腐食モニタリング手法についての平易な解説をする。

東京工業大学金属工学科 沼田 博雄

2. 金属の不動態皮膜について

皮膜破壊現象とその理論、特に破壊に及ぼす電圧の影響、皮膜自体の耐食性、皮膜の半導体的特性と腐食との関連性等について解説する。

北海道大学工学部 佐藤 教男

3. パネルディスカッション

パネラー 高橋正雄, 石川達雄, 杉本克久, 加藤正義

講演 1 の沼田氏は最近 Texas A and M Univ. の Prof. Bockris の下で 2 年間溶融塩腐食の研究をしてこられた新進の化学者である。本講演では溶融塩中における金属の腐食研究が、新エネルギー源の開発に関連して最近特に重要視されてきたことが強調された。そしてこの腐食系でも水溶液中におけると同様に、混成電位説に従うことが示され、また熱力学的データからいろいろな系で

の電位-pO₂ 線図が紹介され、その有用性が指摘された。また各種プラントや原子炉における腐食速度のモニタリングの重要性が述べられ、アノード分極特性、分極抵抗および交流式腐食モニター法の溶融塩系への適用例が数多く紹介された。これに対する討議として石川教授より「分極時の電流は溶融塩の酸化、還元電流なのか、金属の溶解、析出電流なのか、その中味を知る必要がある」というコメントが出された。高橋教授は、溶融塩の塩基度と酸素/超氧化物イオン/過氧化物イオン/酸化物イオン間の平衡図について説明され、この平衡が第二世代燃料電池の酸素極の反応機構と関連して重要であることを指摘された。杉本教授は合金系の表面皮膜は深さ方向に不均一で多層構造となり、組成、結晶構造によって厚さが異なることを電顕写真によって示された。

講演 2 の佐藤教授は昨年米国電気化学会より、Outstanding Achievement Award of the Corrosion Division を受賞されたので、今回はその内容の一部を紹介して頂いた。その内容は、1. 金属表面不動態皮膜、2. 表面電気二重層、3. 皮膜の溶解、4. 皮膜の破壊より成り、各項目について演者の永年にわたる研究成果が平易に解説された。1 では皮膜は厚さ 0.5~5 nm 程度の非晶質あるいはガラス状の酸化物および含水酸化物で、高密度な構造欠陥を含む半導体あるいは絶縁体とみられること、2 では電気二重層の電位差が液の pH に依存する一定値をとるが、その電位分布はまだ明確ではない等の説明があった。3 では酸化物の自然溶解はヘルムホルツ層の電位差に支配されることや酸化物皮膜の電気化学的分解の機構が述べられ、4 では全面破壊と局部破壊の機構の説明があり、特に電圧応力による絶縁破壊現象の説明は興味深かった。

最後に岡本教授が不動態研究に対するコメントを出され「この研究は皮膜の Surface Characterization だけでは不十分であり、もっと溶液中の on site での動的挙動、特に皮膜の self repairing に注目する必要がある」ことを強調された。

(本会腐食専門委員会委員長 加藤正義)