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Corrosion Protect DLC Coating on Steel and Hastelloy

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The electrochemical behaviors of coating films on the steel and Ni–Cr–Mo alloy (Hastelloy) were investigated to obtain fundamental data on their corrosion resistance characteristics. We compared several types of materials and coating layers. SUS316, Hastelloy, DLC (Diamond-like carbon) on SUS316 and DLC on Hastelloy samples showed stable potential-time characteristics. F_2 processing SUS316 and F_2 processing Hastelloy samples showed negative direction change of the potential, and an active dissolution peak appeared in the F_2 processing SUS316 samples. On the other hand, DLC samples on SUS316 and Hastelloy showed a small anode current. It appeared that DLC coating was a superior resistance layer for the corrosion. [doi:10.2320/matertrans.MRA2007301]

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1. Introduction

The metal-insulator-metal (MIM) capacitor with high-k dielectric layer is focused in the dynamic random access memory (DRAM) storage node. Hf-based High-k materials have been recently adopted to the mass production as capacitors in memory devices because of their higher dielectric constant. HfO_2 has a dielectric constant of k~25, and is deposited by the atomic layer deposition (ALD) method. In-situ chamber cleaning is a crucial technology for improvement of productivity and yield in the device manufacturing. Dry cleaning is performed in the chamber cleaning at the interval of several deposition cycles to avoid film cracking or peeling from the chamber wall. However, HfO_2 is extremely difficult to etch by dry cleaning. A few studies have been concerned with the plasma etching of high-k dielectrics. Sha *et al.*[1] investigated the etching of ZrO_2 in ECR plasma with BCl_3/Cl_2. Kitagawa *et al.*[2] studied the etching of HfO_2 by ECR plasma with BCl_3/O_2. Recently, thermal BCl_3/O_2 etching is proposed for HfO_2 etching.[3] But, BCl_3 is a corrosive gas for steel and an anti-corrosion measures are necessary to apply it to a dry etching process. As an anti-corrosion measure, the metal oxidation method is widely used for the SUS316 surfaces. To form stronger anti-corrosion, coating films like metal alloy or ceramic layers are proposed as the coating materials. In these materials, metal oxides like as TiO_2, PdO_2 and metal nitride like as TiN, CrN, TiCN layers are formed by sputtering or plasma deposition methods. NiP and NiB layers formed by the electroless plating method are also well known as anti-corrosion films because a thick and uniform film is easily obtained. DLC (Diamond-like carbon) is used for a hard coating film in the mechanical tool industry. The anti-corrosion properties of DLC films were investigated by J. Choi *et al.*[4] and it was reported that the Si-incorporated DLC film improved the performance of corrosion protection in the NaCl solution. In this paper, we have investigated several types of corrosion protection coatings including DLC film and compared their anti-corrosion performance in the HCl solution by the potentiodynamic polarization experiment.

2. Experiments

The following types of samples were prepared for the corrosion evaluation by the potentiodynamic polarization experiment. The samples were (1) Low carbon 316 Stainless Steel (SUS316), (2) Ni–Cr–Mo alloy (Hastelloy: Mitsubishi Materials, MA-22), (3) DLC (Diamond-like carbon) coating on SUS316, (4) DLC coating on Hastelloy, (5) F_2 processing SUS316, (6) F_2 processing Hastelloy, and (7) NiF, NiP coating on SUS316. Sample size was (15 mm × 15 mm × 3 mm) and the metal surface was treated by electrical-chemical polishing. For sample (1), the chemical composition of SUS316 was C: 0.015, Si: 0.63, P: 0.03, S: 0.01, Cr: 17.64, Mn: 0.96, Fe: 69.32, Ni: 12.16, Mo: 2.23 (unit: %). For sample (2), the chemical composition of Hastelloy was C: 0.003, Si: 0.03, P: 0.01, S: 0.01, V: 0.02, Cr: 21.30, Mn: 0.20, Fe: 4.50, Co: 0.90, Ni: 56.52, Mo: 13.50, W: 3.00 (%). For sample (3) and (4), DLC film was formed by the plasma based ion implantation (PBII) method using C_7H_8 (toluene).[5] In the PBII process, bipolar pulses were added to the target. After the surface cleaning by Ar sputtering, the ions of glow discharge plasma by a positive pulse (2 kV) were implanted into the target with a subsequent negative voltage pulse (−5 kV). Si contained DLC layer was formed as an interlayer to reduce internal stress. Total DLC film thickness was controlled to 800 nm. DLC film was analyzed by Raman analysis and showed a strong dependence on the physical properties of the ratio of sp^2 (graphitelike) to sp^3 (diamond-like) bonds. From the raman spectra of DLC film, two sharp modes were observed, and these peaks were G peak at 1550 cm^{-1} and D peak at 1380 cm^{-1}. After the spectra fitting, the area of G band and D band was compared and I_D/I_G was calculated as 1.15. For sample (5) and (6), F_2 processing SUS316 and Hastelloy samples were prepared by F_2 gas annealing at 225°C, 50 torr for 2 hours in a conventional vertical furnace. For sample (7), NiF/NiP layers were formed by the electroless plating method. The NiP layer was coated by 20 µm on SUS316, and the following NiF layer was formed by thermal treatment in a F_2 gas ambient. The potentiodynamic polarization experiments were conducted to evaluate the corrosion performance of samples in an aqueous

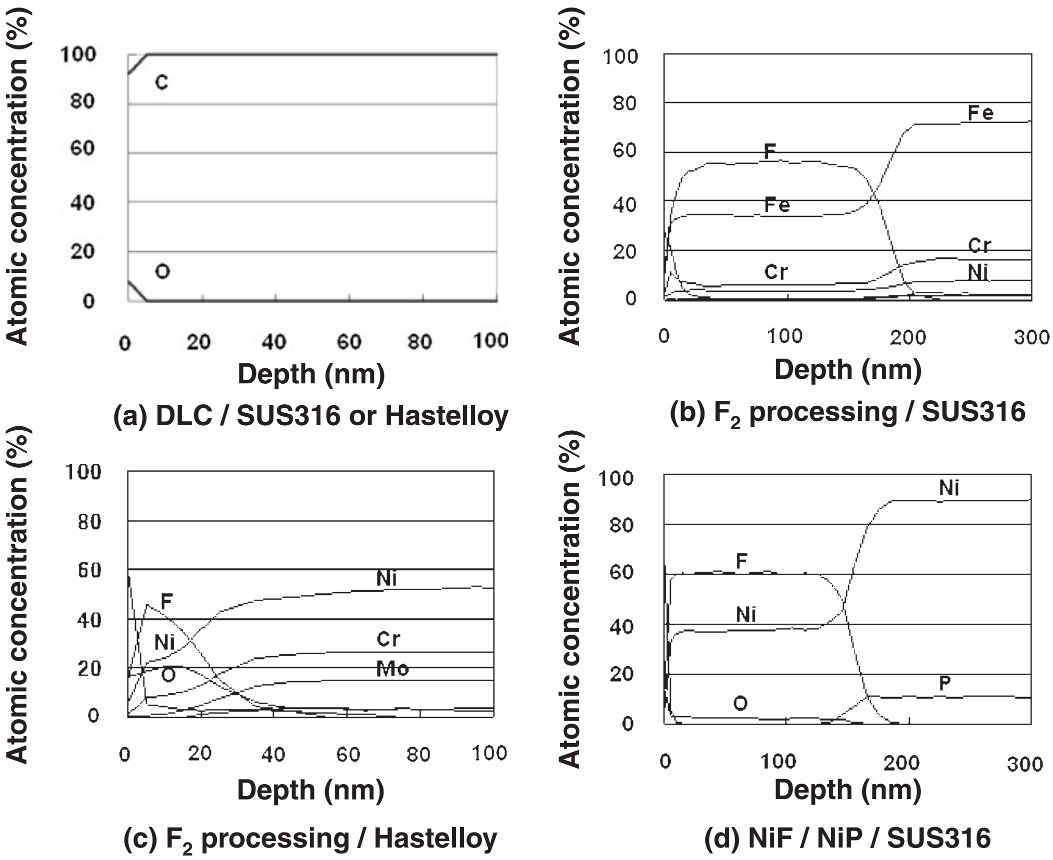

Fig. 1 XPS depth profiles samples for (a) DLC/SUS316 or Hastelloy, (b) F_2 processing of SUS316, (c) F_2 processing of Hastelloy, and (d) NiF/NiP/SUS316.

0.01 M/dm^3 (pH2) HCl solution at 35°C. Sample surface was masked by the insulator except the measurement area of (7 mm × 7 mm). Anode and cathode polarization characteristics were measured by multisweep voltammetry at a scanning rate of 20 mV/min with a conventional three-electrode system. The corrosion current density and the corrosion rate were settled from the extrapolation of the polarization curve. And the corrosion rates of the coating films on SUS316 substrate samples were converted by the SUS316 corrosion rate, and also Hastelloy substrate samples were converted by the Hastelloy corrosion rate. Pt and a Saturated Calomel Electrode (SCE) were used for the counter and the reference electrode. The compositions of these samples were measured by X-ray photoelectron spectroscopy (XPS: PHI Quantera SXM) for an area of 100 μm diameter. Using Al-Xray source (1486.6 eV), the spectra was obtained at the angle of 45° with Ar sputtering (2.0 kV). After the corrosion test, samples were observed using the scanning electron microscopy (SEM).

3. Results and Discussion

Halogen gases such as hydrogen chloride (HCl), boron trichloride (BCl_3), fluorine (F_2), nitrogen trifluoride (NF_3), and chlorine trifluoride (ClF_3) are used as etching gases in semiconductor processes. Halogen gases are easily hydrolyzed in an atmosphere and the metal surface of the reaction chamber is corroded by generating chloride or fluoride. It was reported that the electrical-chemical polished stainless steel SUS316 did not have corrosion resistance and a nickel alloy was adopted for the corrosion resistance material. Though Ni–Cr–Mo alloy (Hastelloy) shows a superior corrosion resistance, under a high temperature condition, the surface becomes corroded. It is known that the metal surface reacts with fluorine ($\chi = 3.98$) or oxygen ($\chi = 3.44$) which has a large electronegativity (χ) and changes to a chemically stable structure. F_2 etching gas reacts with Iron (Fe), Chromium (Cr), Nickel (Ni) on SUS316 surface and forms metal fluorides. We tried to apply metal fluoride as a corrosion resistance film.

The chemical compositions of the coating films were analyzed by XPS. Figure 1 shows the depth profile results of (a) DLC/SUS316 or Hastelloy (Sample 3, 4), (b) F_2 processing SUS316 (sample 5), (c) F_2 processing Hastelloy (sample 6) and (d) NiF/NiP on SUS316 (sample 7) respectively. From Fig. 1(a), DLC film shows the composition of 100% carbon except for 5 nm from the surface. The composition of the F_2 processing SUS316 (sample 5) is Fe: 33.9, Cr: 6.0, Ni: 3.6, Mo: 0.4, F: 56.1 (%) and the composition of F_2 processing Hastelloy (sample 6) is Cr: 8.8, Ni: 24.0, Mo: 1.0, F: 41.5, O: 20.7, C: 4.0 (%). Though F_2 processing time is both 2 hours for sample 5 and 6, fluorine diffusion depth is 200 nm for SUS316 and 40 nm for Hastelloy. This fact shows it is comparably easy to form Fe–F bonding for SUS316 but it is not easy to make Ni–F, Mo–F or Cr–F bonding for hastelloy. O peak in Hastelloy is

Table 1 Chemical composition for SUS316, Hastelloy and coating films.

No.	Sample	C	O	F	Si	P	S	V	Cr	Mn	Fe	Co	Ni	Mo	W
1	SUS316	0.015	—	—	0.63	0.03	0.01	—	17.64	0.96	66.32	—	12.16	2.23	—
2	Hastelloy	0.003	—	—	0.03	0.01	0.01	0.02	21.30	0.20	4.50	0.90	56.52	13.50	3.00
3	DLC (DLC/SUS316)	100.0	—	—	—	—	—	—	—	—	—	—	—	—	—
4	DLC (DLC/Hastelloy)														
5	F_2 processing SUS316	—	—	56.1	—	—	—	—	6.0	—	33.9	—	3.6	0.4	—
6	F_2 processing Hastelloy	4.0	20.7	41.5	—	—	—	—	8.8	—	—	—	24.0	1.0	—
7	NiF (NiF/NiP/SUS316)	—	2.0	61.0	—	—	—	—	—	—	—	—	37.0	—	—
	NiP (NiF/NiP/SUS316)	—	—	—	—	11.0	—	—	—	—	—	—	89.0	—	—

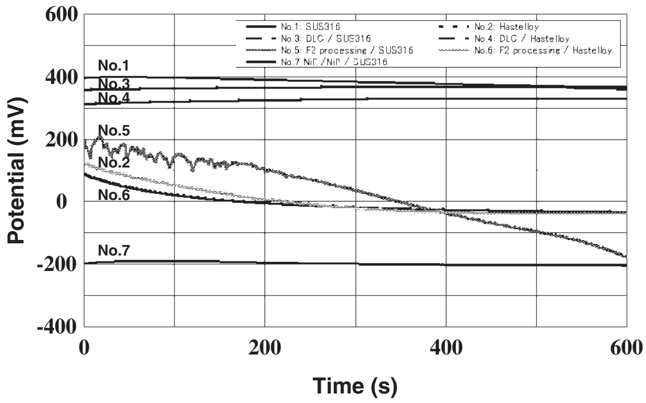

Fig. 2 Rest potential-time curve in HCl solution for 10 min.

formed with Ni when the sample is loaded into the process chamber. From the profile of (c) NiF/NiP on SUS316, the composition of NiF layer is defined Ni: 37.0, F: 61.0, O: 2.0 (%) and NiP layer is defined Ni: 89.0, P: 11.0 (%) respectively. The chemical compositions of the coating films are summarized in Table 1. These values are analyzed at 50 nm depth from the surface for DLC coating samples (sample 3, 4), F_2 processing SUS316 (sample 5), NiF layer of NiF/NiP/SUS316 (sample 7), and at 10 nm depth for F_2 processing Hastelloy (sample 6), and at 200 nm depth for NiP layer of NiF/NiP/SUS316 (sample 7).

Before the polarization curve measurement, we measured the rest potential-time curve in HCl solution for 10 min as in Fig. 2. This curve shows the dissolution stability of the metals in the electrolysis solution. SUS316 (sample 1), DLC/SUS316 and DLC/Hastelloy samples (sample 3, 4) show a positive potential at $300 \sim 400$ mV (based on SCE). Hastelloy (sample 2) shows the potential of $-50 \sim 0$ mV, NiF/NiP/SUS316 (sample 7) shows $-150 \sim -200$ mV and the rest potential-time curves are relatively stable in the HCl solution. On the other hand, the rest potential-time curve of the F_2 processing SUS316 (sample 5) and F_2 processing Hastelloy (sample 6) samples shift to the negative potential, and the potential change is especially large for the F_2 processing SUS316 sample (sample 5). From the results, it seems that the F_2 processing SUS316 (sample 5) and F_2 processing Hastelloy (sample 6) have a dissoluble layer in the HCl solution.

Figure 3 shows the potentiodynamic curves obtained from the potentiodynamic polarization experiments. The current density is the total current of the anodic and cathodic currents. The active dissolution peak appeared in the F_2 processing SUS316 (sample 5) sample. On the other hand, SUS316 (sample 1), Hastelloy (sample 2), DLC/SUS316 (sample 3), DLC/Hastelloy (sample 4), NiF/NiP on SUS316 (sample 7) are shown in the passive state. DLC samples especially show a small anode current and superior resistance for corrosion. The corrosion current density and corrosion rate by Tafel analysis are shown in Table 2. F_2 processing samples (sample 5, 6) have a higher corrosion rate compared to the SUS316 or Hastelloy materials. The corrosion rate of DLC coating is one order of magnitude or more smaller, compared to the other coating materials and show superior resistance to corrosion. NiF/NiP/SUS316 (sample 7) has 1/3 of the corrosion rate of SUS316 (sample 1) sample.

After corrosion tests, the sample surfaces of the anode electrode were observed using SEM as shown in Fig. 4. The surfaces of SUS316, DLC/SUS316 F_2 processing SUS316 (sample 1, 3, 5) are etched and several holes are observed. In the case of Hastelloy, DLC/Hastelloy, F_2 processing Hastelloy (sample 2, 4, 6) surfaces, a lot of cracks, pits and deposits are observed. From the SEM results, it is cleared that the anode electrode surface is different between the SUS316 and Hastelloy substrate. The deposits on Hastelloy substrate are Mo and W oxides from XPS analysis. And it is confirmed that MoO_2, MoO_3 or WO_2, WO_3 compounds are formed at the condition of the noble potential and pH2 from the potential–pH equilibrium chart for Mo–H_2 or W–H_2 system. The results of XPS analysis and the potential–pH equilibrium chart corresponds for the deposits on Hastelloy substrate. From Fig. 4, there are no differences between the SEM photographs after the potentiodynamic polarization experiments by the type of films on the same substrate. But it is cleared that SUS316 and Hastelloy show different etching pit shape. Also, Hastelloy forms Mo-oxide compounds easily. It should be considered when selecting a coating substrate.

4. Conclusion

Anti-corrosion properties were investigated by using the potentiodynamic polarization experiments in the HCl solution of pH2. In the several types of materials and coating layers, SUS316, Hastelloy, DLC on SUS316, DLC on Hastelloy samples, show stable rest potential-time characteristics. F_2 processing SUS316 and F_2 processing Hastelloy samples show a negative direction change of potential. And

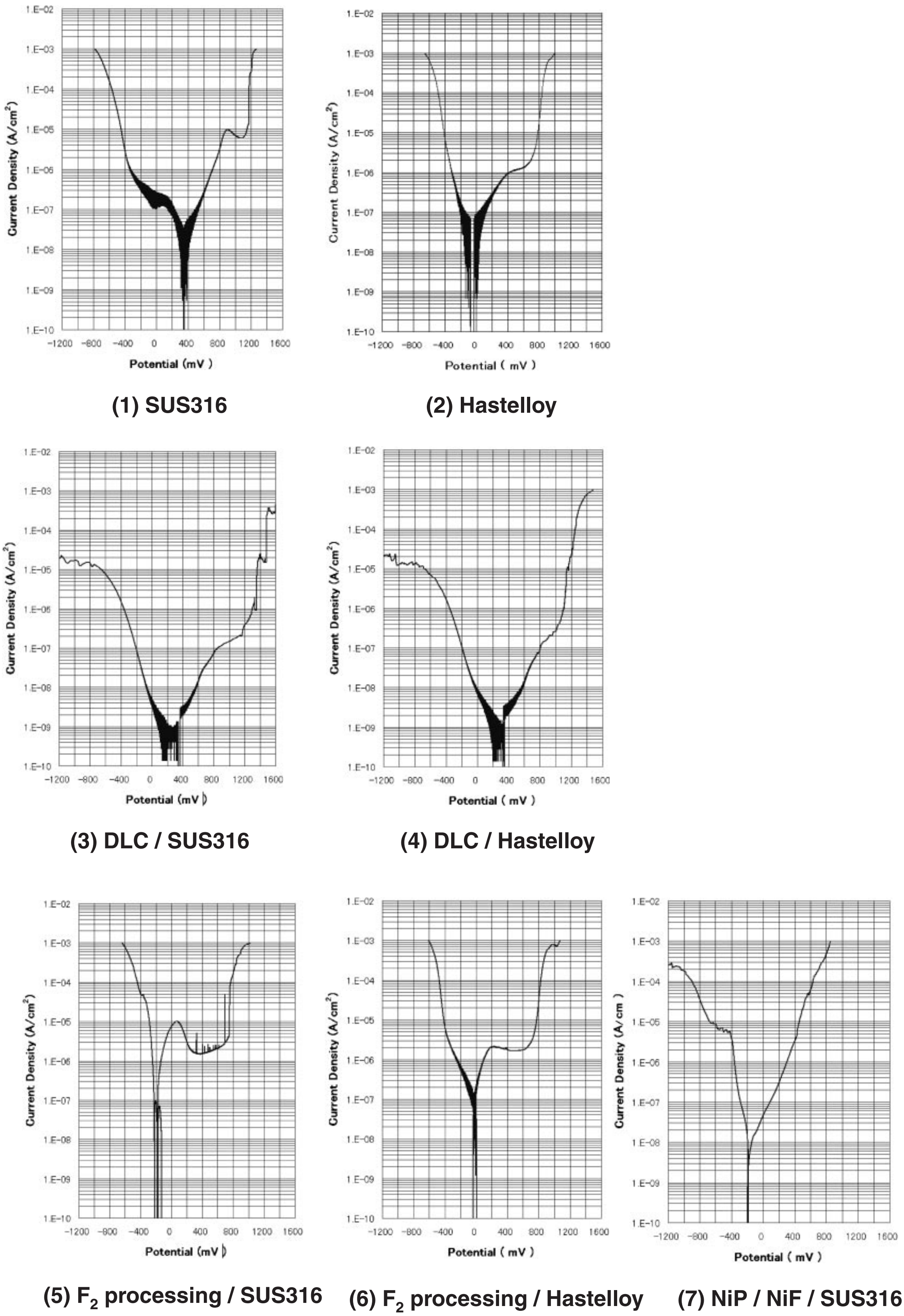

Fig. 3 Polarization curve for coating films.

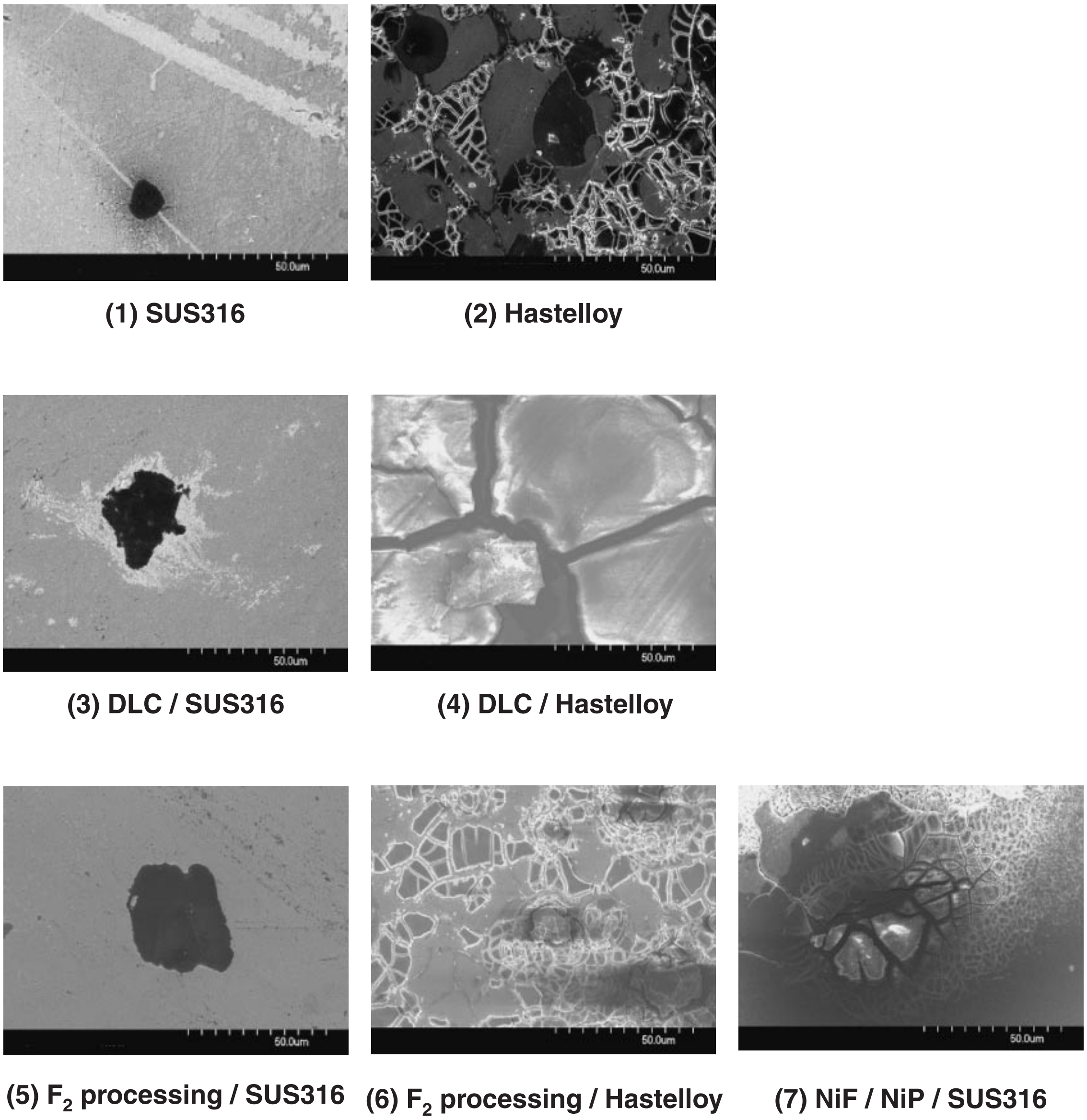

Fig. 4 SEM observation for anode electrode after Potentiodynamic polarization experiments.

Table 2 Current Density and Corrosion Rate for coating films.

No.	Sample	Current Density (A/cm^2)	Corrosion Rate (μm/year)
1	SUS316	2.5×10^{-8}	0.26
2	Hastelloy	5.0×10^{-8}	0.49
3	DLC/SUS316	1.0×10^{-9}	0.01
4	DLC/Hastelloy	1.0×10^{-9}	0.01
5	F_2 processing/SDS316	2.5×10^{-6}	26.0
6	F_2 processing/Hastelloy	1.0×10^{-7}	1.0
7	NiF/NiP/SDS316	8.0×10^{-9}	0.08

the active dissolution peak appeared in the F_2 processing SUS316 sample. On the other hand, DLC on SUS316 and DLC on Hastelloy samples show a small anode current, and it is appeared that DLC coating is a superior resistance layer against corrosion in HCl solution.

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