# Electropolishing of 316L Stainless Steel for Anticorrosion Passivation

## H. Hocheng, P.S. Kao, and Y.F. Chen

**316L stainless steel is deemed an indispensable material in the semiconductor industry. In many instances, the surface of the production equipment needs to be treated for low-corrosion passivation, good finish, weldability, and cleanliness. The process characteristics of electropolishing meet these requirements well. The current study investigates the effects of the major processing parameters on the anticorrosion performance and the surface roughness. The electrolyte with 10% water content and a ratio between $H_2SO_4$ and $H_3PO_4$ of 4 and 6 has been proven to be successful, showing no corrosion pitting points on the specimen surface. The electrolyte temperature of $85 \pm 10$ °C and the electrical current density of 0.5 to 1.0 $A/cm^2$ are found to be optimal. The processing time beyond 3 to 5 min produces no further improvement. The addition of 10% glycerin provides a very fine surface (maximum roughness of 0.05 $\mu$m), while the anticorrosion performance is deteriorated. The results obtained are useful for the manufacture of the semiconductor equipment.**

## 1. Introduction

Electrochemical machining (ECM) was first introduced in 1929 by Gusseff; later it was found that ECM is particularly advantageous for high-strength and high-melting-point alloys. Industrial applications have been extended to electrochemical drilling, electrochemical deburring, electrochemical grinding, and electrochemical polishing.[1] Electropolishing is based on the principle of anode metal dissolution in the electrolyte described by Faraday's law. Good surface brightness and a stress-free surface can be obtained by electropolishing.[2]

The effects of electropolishing of a workpiece immersed in an electrolyte tank are threefold.

(1) Micropolishing: The removal of the microbulge on the surface of about 0.01 mm in height makes the surface more reflective and bright, while the smoothness of the surface might not be improved. (2) Macropolishing: The removal of the bulge of larger than 0.1 mm in height smoothes the surface, while the brightness of the surface is not guaranteed. (3) Passivation: Electropolishing produces a chemically passivated layer (particularly suitable for stainless steel and copper) that other mechanical polishing processes cannot achieve. The formation mechanism of the passivation layer on the anode during electropolishing has not been fully analytically explored, while its application has been called "anodic protection," so named by Edeleanu in 1954. The corrosion rate of metal slows down $10^3$ to $10^6$ times when passivation occurs. Chromium, iron, nickel, and titanium show this behavior very well. Table 1[3] shows the passivation performance of a 304 stainless steel as an illustrative

**H. Hocheng** and **P.S. Kao,** Department of Power Mechanical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China; and **Y.F. Chen,** Mechanical Industrial Research Laboratory, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China. Contact e-mail: hocheng@pme.nthu.edu.tw.

example. The specification of a passivated layer can be described as follows: (1) the quantity of chromium in that layer is 1.5 times greater than iron; or (2) the quantity of the oxidized chromium doubles the quantity of oxidized iron; or (3) the thickness of the oxidized layer is larger then 2 nm.

The effect of electropolishing is in general better than that of mechanical polishing, and the polished surface can reach the mirror-class finish. Besides, by removing the layer associated with stress concentration, oxygen, hydrogen, carbon, and other impurities, this technique achieves ultrafine cleanliness and is beneficial for subsequent welding. It can hardly grow a germ on the electropolished surface. These characteristic merits fit the needs of the semiconductor industry well, because this industry requires fine surface roughness, top class cleaning, good passivation, easy welding, retardant chemical reactivity, and high dimensional precision. The material used for parts in the semiconductor industry is generally stainless and possesses a large amount of the above-mentioned elements (chromium, *etc.*). An example of a part used in the semiconductor industry is a mass and flow control valve. This part should be electropolished to obtain the surface roughness and passivation layer required for application.

This paper investigates the passivation processing of the 316 stainless steel used in the semiconductor industry, where the parts have to be electropolished after machining. The polished surface has to exhibit a predetermined corrosion resistance and a maximum surface roughness of below 0.8 $\mu$m. The performance of the anode protection is affected by the compositions, temperature, and concentration of the electrolyte. The purpose of this research is to pursue the suitable conditions of passivation processing to meet the requirements for the semiconductor industry.

## 2. Experimental Setup

### 2.1 Passivation Processing

The experimental setup is composed of a power supply, current meter, voltage meter, stainless steel container, work-
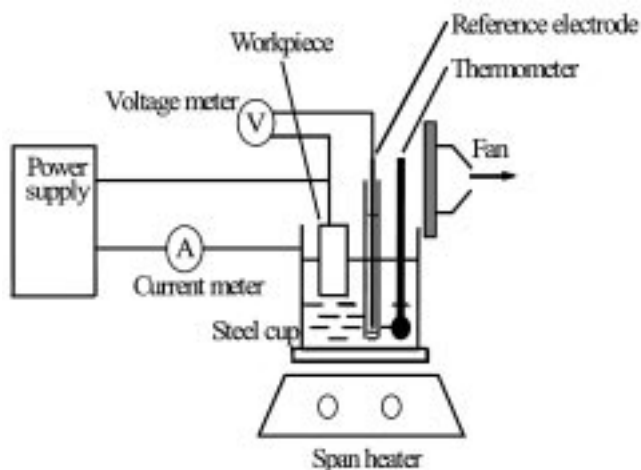
**Fig. 1** Sketch of experimental setup of surface passivation



**Fig. 2** Sketch of experimental setup of corrosion test

**Table 1  Passivation performance of 304 stainless steel[3]**

| | | Corrosion rate (mill/year) | |
| --- | --- | --- | --- |
| Alloy type | Environment (exposed to air) | Unprotected | Anode protected |
| 304 (19Cr-9Ni) | $N$ $H_2SO_4$ + $10^{-5}M$ NaCl | 14 | 0.025 |
| | $N$ $H_2SO_4$ + $10^{-3}M$ NaCl | 2.9 | 0.045 |
| | $N$ $H_2SO_4$ + $10^{-1}M$ NaCl | 3.2 | 0.20 |
| | 10 $N$ $H_2SO_4$ + $10^{-5}M$ NaCl | 1930 | 0.016 |
| | 10 $N$ $H_2SO_4$ + $10^{-3}M$ NaCl | 1125 | 0.04 |
| | 10 $N$ $H_2SO_4$ + $10^{-1}M$ NaCl | 77 | 0.21 |

**Table 2  Experimental conditions**

| | |
| --- | --- |
| Electrolyte temperature (°C) | 50/60/70/80/90 |
| Current density (A/cm$^2$) | 0.5/0.75/1.0/1.25/1.5/2.0/2.5/3.0 |
| $H_2SO_4$:$H_3PO_4$ | 5:5/4:6/3:7 |
| Water content (%) | 0/10/20/30 |
| Time (min) | 3/6/9 |
| Glycerin (%) | 0/10 |

piece, reference electrode, thermometer, fan, and stirring heating apparatus. A schematic diagram of the experimental setup is shown in Fig. 1.

The power supply provides the direct current of maximum 180 A. The stainless steel container avoids the ferromagnetism. The experimental sample is 316L stainless steel of 30 mm length, 1 mm thickness, and 20 mm width. The reference electrode uses the Cu-CuSO$_4$ half battery. Before the experiment proceeds, the phosphoric acid, sulfuric acid, glycerin, and water are added at the designed ratio. The electrolyte is heated to the experimental temperature and stirred. The workpiece is immersed into the electrolyte 20 mm deep, and connected to the current. The experimental conditions are listed in Table 2.

### 2.2 Corrosion Test

The method of the corrosion test conforms to ASTM G48. It can discriminate the passivation level among different passivation layers, and is considered suitable for assessing the effects of the processing parameters in the experiment.

Figure 2 shows the experimental setup of the corrosion test. The workpiece is put into the FeCl$_3$ solution 2 cm deep. The container is then sealed, and the temperature is controlled at 50 °C for 72 h.

## 3. Results and Discussion

Tables 3 and 4 and Fig. 3 and 4 show the effects of various processing parameters on the anticorrosion performance. The produced surface finish is also observed. The maximum and average surface roughness are measured only on the bright polished surface by a testing device. The values are included in the tables of results.

### 3.1 Effects of Electrical Current and Temperature

As shown in Fig. 3, the passivation is strongly affected by the current, and a temperature of 60 to 75 °C is considered a threshold. When the temperature is lower then 60 °C, higher electrical current density produces better passivation against corrosion. However, at a temperature higher then 75 °C, the strong current worsens the passivation effect. The specification of a passivation layer is described in Section 1. In general, this higher temperature with adequate current density produces the best corrosion resistance and a satisfactory surface finish. At 50 to 60 °C, the best passivation occurs at a current density of 2.5 A/cm$^2$. At 75 to 95 °C, the best passivation occurs at 0.5 to 1.0 A/cm$^2$. In both cases, the number of the corroded points

**Table 3  Number of pitting points and surface finishes without glycerin (water 10%)**

| (a) $H_2SO_4:H_3PO_4$ = 5:5 Electrolyte temperature °C | | | | |
|---|---|---|---|---|
| 50 | 60 | 75 | 85 | 95 |
| Current Density (A/cm$^2$) | | | | |
| 0.5  8 (dull) | 5 (dull) | 1 (dull) | 0 $R_{max}$ = 3.13 $\mu$m, $R_a$ = 0.3 $\mu$m | 0 $R_{max}$ = 3.2 $\mu$m, $R_a$ = 0.22 $\mu$m |
| 1.0  5 (dull) | 4 (dull) | 1 (dull) | 2 (dull) | 2 (dull) |
| 1.5  4 (dull) | 3 (dull) | 5 (dull) | … | … |
| 2.0  2 (dull) | 2 (dull) | 10 (dull) | … | … |
| 2.5  1 (dull) | 0 (dull) | … | … | … |
| (b) $H_2SO_4:H_3PO_4$ = 4:6 Electrolyte temperature °C | | | | |
| 50 | 60 | 75 | 85 | 95 |
| Current Density (A/cm$^2$) | | | | |
| 0.5  … | … | 4 (dull) | 0 $R_{max}$ = 2.4 $\mu$m, $R_a$ = 0.19 $\mu$m | 2 (dull) |
| 0.75  … | … | 1 (dull) | 0 $R_{max}$ = 1.4 $\mu$m, $R_a$ = 0.11 $\mu$m | 1 (dull) |
| 1.0  8 (dull) | 7 (dull) | 0 $R_{max}$ = 1.7 $\mu$m, $R_a$ = 0.21 $\mu$m | 0 $R_{max}$ = 0.8 $\mu$m, $R_a$ = 0.08 $\mu$m | 1 (dull) |
| 1.25  8 (dull) | 5 (dull) | 0 $R_{max}$ = 1.1 $\mu$m, $R_a$ = 0.28 $\mu$m | 1 (dull) | 1 (dull) |
| 1.5  4 (dull) | 4 (dull) | … | … | … |
| 2.0  2 (dull) | 2 (dull) | … | … | … |
| 2.5  0 $R_{max}$ = 1.0 $\mu$m, $R_a$ = 0.2 $\mu$m | 2 (dull) | … | … | … |
| 3.0  4 (dull) | 4 (dull) | … | … | … |
| (c) $H_2SO_4:H_3PO_4$ = 3:7 Electrolyte temperature °C | | | | |
| 50 | 60 | 75 | 85 | 95 |
| Current Density (A/cm$^2$) | | | | |
| 0.5  … | … | 1 (dull) | 2 (dull) | 0 $R_{max}$ = 3.1 $\mu$m, $R_a$ = 0.28 $\mu$m |
| 0.75  … | … | 1 (dull) | 1 (dull) | 0 $R_{max}$ = 2.4 $\mu$m, $R_a$ = 0.19 $\mu$m |
| 1.0  8 (dull) | 5 (dull) | 1 (dull) | 1 (dull) | 2 (dull) |
| 1.25  8 (dull) | 5 (dull) | 2 (dull) | 2 (dull) | 2 (dull) |
| 1.5  10 (dull) | 6 (dull) | … | … | … |
| 2.0  5 (dull) | 2 (dull) | … | … | … |
| 2.5  1 (dull) | 0 $R_{max}$ = 2.0 $\mu$m, $R_a$ = 0.2 $\mu$m | … | … | … |
| 3.0  2 (dull) | 0 $R_{max}$ = 1.7 $\mu$m, $R_a$ = 0.19 $\mu$m | … | … | … |

is found to be zero when the ASTM G48 test norm is used. When the current density is over 1 A/cm$^2$, there are many pitting points on the workpiece, and a rough surface is produced. When the current density is insufficient (0.5 A/cm$^2$), both the surface finish and the brightness of the workpiece are unsatisfactory.

### 3.2 Effects of Acid Ratio

When the ratio between $H_2SO_4$ and $H_3PO_4$ is set from 5:5 to 4:6, the number of the corroded points reduces obviously, as shown in Fig. 3. There is a chance to reduce the corroded points to zero when the current density is set between 0.5 and 1.25 A/cm$^2$ (at 75 °C and 1 to 1.25 A/cm$^2$ or 85 °C and 0.5 to A/cm$^2$). However, the trend of the effects of electrolyte temperature and current density remains the same (85 to 95 °C, 0.5 A/cm$^2$). The surface roughness of $H_2SO_4:H_3PO_4$ = 4:6 is better than $H_2SO_4:H_3PO_4$ = 5:5. For example, the maximum surface roughness is reduced from 3.1 to 2.4 $\mu$m at 85 to 95 °C and 0.5 A/cm$^2$. When the current is larger then 1.5 A/cm$^2$, pitting happens as before.

As the ratio between $H_2SO_4$ and $H_3PO_4$ is further tuned to 3:7, the results of the corrosion resistance show the same trend, while the surface roughness is worse compared to that of $H_2SO_4:H_3PO_4$ = 4:6.

### 3.3 Effects of Water Content

Figure 4 shows that 10% water content is optimal for passivation. The water content of less than 10% produces more corroded points, while the water content of more than 10% increases the corroded points rapidly. From 10 to 20%, the number of corroded points increases from 5 to 7, and the further increase in water content causes a huge amount of pitting points on the surface of the workpiece. The best condition of the water content is 10%.

### 3.4 Effects of Polishing Time

Between 3 and 9 min, the polishing time has little or a negative effect on passivation, as shown in Fig. 4. Three minutes for processing is recommended in order to save time and expense.

### 3.5 Effects of Glycerin

When comparing Table 3 and 4, one finds that adding glycerin into the solvent increases the number of corroded points on the workpiece, particularly at high temperature. Table 4 further shows there is no noncorroded sample (zero pitting point) in the conditions of $H_2SO_4:H_3PO_4$ = 4:6 and 3:7. However, the surface roughness is improved with added glycerin. The best surface roughness can be achieved with glycerin (namely, $R_{max}$ = 0.44 $\mu$m and $R_a$ = 0.05 $\mu$m, Table 4b).
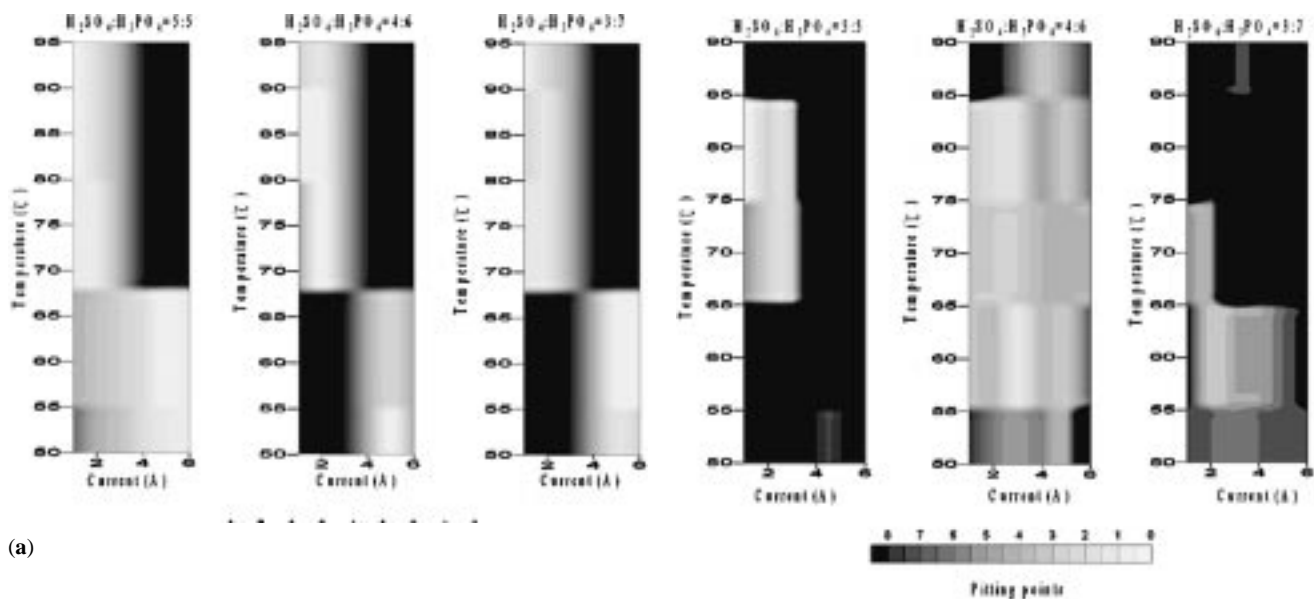
**Fig. 3** Effects of sulfuric acid concentration, temperature, and current: (**a**) without glycerin and (**b**) with glycerin

**Table 4  Number of pitting points and surface finishes with 10% glycerin (water 10%)**

| (a) $H_2SO_4:H_3PO_4 = 5:5$ Electrolyte temperature °C | | | | |
|---|---|---|---|---|
| 50 | 60 | 70 | 80 | 90 |
| Current Density (A/cm²) | | | | |
| 0.5 ... | ... | 2 (dull) | 0 $R_{max} = 3.1$ $\mu$m, $R_a = 0.28$ $\mu$m | 4 (dull) |
| 0.75 ... | ... | 0 $R_{max} = 3.1$ $\mu$m, $R_a = 0.28$ $\mu$m | 1 (dull) | 0 $R_{max} = 3.1$ $\mu$m, $R_a = 0.28$ $\mu$m |
| 1.0 ... | ... | 1 (dull) | 1 (dull) | 6 (dull) |
| 2.5 3 (dull) | 4 (dull) | ... | ... | ... |
| 3.0 4 (dull) | 4 (dull) | ... | ... | ... |

| (b) $H_2SO_4:H_3PO_4 = 4:6$ Electrolyte temperature °C | | | | |
|---|---|---|---|---|
| 50 | 60 | 70 | 80 | 90 |
| Current Density (A/cm²) | | | | |
| 0.5 8 (dull) | 3 (dull) | 3 $R_{max} = 1.28$ $\mu$m $R_a = 0.14$ $\mu$m | 3 $R_{max} = 1.93$ $\mu$m $R_a = 0.26$ $\mu$m | 24 (dull) |
| 1.0 6 (dull) | 4 (dull) | 3 $R_{max} = 1.64$ $\mu$m $R_a = 0.13$ $\mu$m | 2 $R_{max} = 1.78$ $\mu$m $R_a = 0.17$ $\mu$m | 10 (dull) |
| 1.5 5 (dull) | 1 $R_{max} = 0.85$ $\mu$m, $R_a = 0.07$ $\mu$m | 3 (dull) | 2 (dull) | 6 (dull) |
| 2.0 6 (dull) | 4 (dull) | 4 (dull) | 5 (dull) | 3 (dull) |
| 2.5 4 $R_{max} = 0.63$ $\mu$m, $R_a = 0.06$ $\mu$m | 3 $R_{max} = 0.44$ $\mu$m, $R_a = 0.05$ $\mu$m | 4 (dull) | 3 (dull) | 5 (dull) |
| 3.0 18 (dull) | 7 (dull) | 4 (dull) | 6 (dull) | 8 (dull) |

| (c) $H_2SO_4:H_3PO_4 = 3:7$ Electrolyte temperature °C | | | | |
|---|---|---|---|---|
| 50 | 60 | 70 | 80 | 90 |
| Current Density (A/cm²) | | | | |
| 0.5 8 (dull) | 9 (dull) | 6 $R_{max} = 1.95$ $\mu$m, $R_a = 0.2$ $\mu$m | 44 $R_{max} = 1.97$ $\mu$m, $R_a = 0.24$ $\mu$m | 20 (dull) |
| 1 7 (dull) | 3 (dull) | 5 $R_{max} = 0.9$ $\mu$m, $R_a = 0.11$ $\mu$m | 9 $R_{max} = 0.97$ $\mu$m, $R_a = 0.12$ $\mu$m | 10 (dull) |
| 1.5 6 (dull) | 5 (dull) | 20 (dull) | 15 (dull) | 8 (dull) |
| 2 7 (dull) | 5 $R_{max} = 0.51$ $\mu$m, $R_a = 0.057$ $\mu$m | 12 (dull) | 10 (dull) | 9 (dull) |
| 2.5 7 (dull) | 7 (dull) | 12 (dull) | 14 (dull) | 18 (dull) |

## 4. Conclusions

Based on the results of the experimental investigation, the effects of the electrolyte temperature, electrical current density, water content, acid ratio, and glycerin are reported. One finds that the ideal passivation can be achieved at the temperature over 70 °C and the electrical current near the condition for a bright polished surface. Good passivation is obtained at a
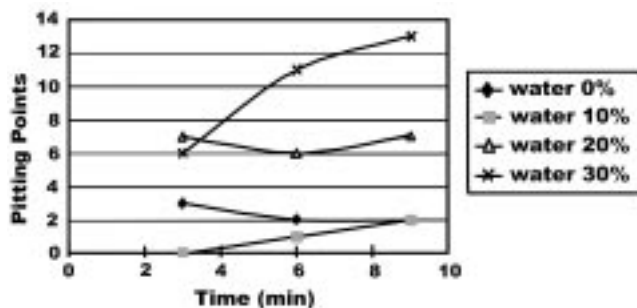
**Fig. 4** Effects of water content and processing time on number of pitting points ($H_3SO_4$:$H_3PO_4$ = 4:6, 85 °C, and 0.75 A/cm$^2$)

temperature below 60 °C and a current density of 2.5 A/cm$^2$, or at a temperature higher than 75 °C and a current density of 0.75 to 1.0 A/cm$^2$. When the temperature is below 60 °C, the passivation is mostly unsatisfactory except that the current density is over 2.5 A/cm$^2$. The electrolyte temperature and current density show the major influence on the corrosion resistance in this experiment. The water content of 10% is optimal for passivation. Adding more water worsens the passivation. The processing time beyond 3 min has little effect on passivation. The best conditions of anticorrosion processing are electrolyte temperature 85 °C, current density 1.0 A/cm$^2$, $H_2SO_4$:$H_3PO_4$ = 4:6, water content 10%, and polishing time between 3 and 5 min. The treated surface shows that the corroded pitting point is zero and the surface roughness is $R_{max}$ = 0.8 $\mu$m, which meet the requirements for the parts used in the semiconductor industry. The addition of glycerin contributes

to the surface polishing. The $R_{max}$ is further reduced to 0.63 $\mu$m, but is disadvantageous for the anticorrosion performance. The obtained results are expected to be of practical value for the manufacturing of semiconductor equipment.

## Acknowledgments

## References

1. J. Wilson: *Practice and Theory of Electrochemical Machining*, Wiley Interscience, New York, NY, 1971, pp. 79-161.
2. B.G. Acharya, V.K. Jain, and J.L. Batra: *Precision Eng.*, 1986, vol. 8 (2), pp. 88-96.
3. M.G. Fortana: *Corrosion Engineering*, McGraw-Hill, New York, NY, 1986.

## Selected References

- J. Bannard: *J. Appl. Electro.*, 1977, vol. 7, pp. 267-70.
- P.A. Charlesworth and C. Hobson: *The Electrochemical Manipulation of Stainless and High-Duty Alloys*, Sheet Metal Industries, New York, 1953.
- D.-T. Chin and K.-W. Mao: *J. Appl. Electrochem.*, 1974, vol. 4, pp. 155-61.
- M. Datta and D. Landolt: *Electro. Acta*, 1981, vol. 26 (7), pp. 899-907.
- A. De Silva and J.A. McGeough: *Proc. Inst. Mech. Eng.*, 1986, vol. 200 (B4), pp. 237-46.
- K.P. Rajurkr *et al.*: *J. Mater. Proc. Technol.*, 1992, vol. 35, pp. 83-91.
- O.L. Riggo and C.E. Locke: *Anodic Protection*, Plenum Press, New York, 1981.