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Abstract—The passivation consists of three steps, that is, the baking process, the direct fluoridation and the thermal modification process. Each of the steps was evaluated in terms of surface flatness, chemical composition and structure. The optimum conditions for the fluorine passivation technology of 316L stainless steel are described. The direct fluoridation products formed at the temperature of 320°C or lower have the single-phase composition of FeF₂, while those which were formed at the temperatures of 330°C or higher have the compound-phase composition with FeF₂ and FeF₃. At certain critical temperature (400°C for 316L stainless steel) of the thermal modification, FeF₂ is converted to FeF₃ and disappears completely as the temperature rises. Meanwhile CrF₃ is formed at certain temperature (440°C for 316L stainless steel). The compound-phase composition gets further crystallized as the thermal modification temperature rises. As the crystal growth induces the cracks on the fluoridated film, it is very difficult to form a satisfactory passivation film from the compound-phase composition by thermal modification. It is confirmed that excellent passivation film has been obtained from the single-phase composition by the optimum fluoridation following the optimum thermal modification.

I. INTRODUCTION

PROCESSING equipment for submicron ULSI fabrication, in particular plasma processing equipment, requires corrosion-resistant metal surfaces, which are free of outgassing and capable of periodic in situ cleaning of adsorbed material [1]-[5]. Fluorine passivation process, applied as a metal treatment, was shown to provide such a surface.

The fluoridation mechanism as well as the process steps leading to a well passivated surface film have been discussed in the literature [6]-[12]. Previous articles by the authors [6]-[18] provide information on fluoridated surfaces on several metals. They also show, that the best passivating film on nickel and stainless steel can be formed only by a two-step fluoridation process [6]. The composition of the film formed in the first step, i.e. a direct fluoridation process, depends on material and process temperature. This step normally results in the formation of a nonstoichiometric fluoride. The film is converted to the stoichiometric structure in a second step, i.e. by thermal modification with the heat treatment of the film in nitrogen. The end product, the stoichiometric fluoride film, was shown to have the best passivation performance [6].

The purpose of this work is to pursue the optimization of the previously published methodology [6] for the 316L stainless steel. The optimum condition for a three-step process, composed of baking, direct fluoridation and thermal modification steps was examined. Results will show that each of these steps influences the quality of the final passivating film. This article describes in detail every part of the overall processes. Section II is focused on baking conditions, Section III describes the results of direct fluoridation and Section IV describes the effects of thermal modification with conclusions presented in Section V.

II. OPTIMUM CONDITIONS FOR BAKING

Table I shows the surface roughness of a smoothly-polished 316L stainless steel before and after baking, where these two samples (n₁ and n₂) were treated under the same conditions and the roughness of surfaces were measured at three random points in each piece. Roughness was measured with stylus profilometer (Alpha step 250). Surface roughness is not influenced by baking at 250°C for 6 hours and 440°C for 6 hours, respectively. In Fig. 1 X-ray photoelectron spectroscopies (XPS) of stainless steel surface before and after baking are shown, where chromium migration to the surface is observed after baking and this phenomenon is more pronounced as the baking temperature rises. But one factor affecting the surface roughness of the fluoridated film in passivation processes is the baking temperature as shown in Fig. 2. Figure 2 shows the surface roughness of two samples treated at the different baking temperatures to follow the same fluoridation and thermal modification. Baking at 250°C shows higher roughness value than baking at 440°C. If the baking temperature is lower than the temperature of thermal modification, the crystal structure of the stainless steel itself is changed by chromium transit during the process of thermal modification and occurs roughness. It is confirmed that the optimum condition of baking is the same temperature as the thermal modification in order to obtain the surface flatness.
TABLE I

<table>
<thead>
<tr>
<th>Condition</th>
<th>n_1</th>
<th>n_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Baking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After Baking in N_2 (250°C, 6 hr)</td>
<td>45 51 61 52</td>
<td>40 32 33 35</td>
</tr>
<tr>
<td>After Baking in N_2 (440°C, 6 hr)</td>
<td>36 43 35 38</td>
<td>29 34 34 33</td>
</tr>
</tbody>
</table>

Fig. 1. Depth Profile of XPS spectra from baked surface of 316L stainless steel.

Fig. 2. Relationship between baking and thermal modification temperatures for surface smoothness of passivated film.

Fig. 3. XRD pattern of the fluoridated films of 316L stainless steel surfaces for fluoridation temperature.

Fig. 4. Proportion of FeF_2 and FeF_3 for various fluoridation temperature.

III. OPTIMUM CONDITION FOR FLUORIDATION

Fluoridation products on the well-polished 316L stainless steel surfaces were studied in the temperature ranging from 220°C to 600°C. Fig. 3 shows the results of X-ray diffraction (XRD) of those products from 220°C to 400°C. Evidently, the fluoridation products fluoridated at the temperatures of 320°C or lower have the single-phase structure while those fluoridated at the temperatures of 330°C or higher have the compound-phase composition consisting of FeF_2 and FeF_3. Figure 4 shows the ratio of integral intensity of FeF_3 and FeF_2 at the fluoridation temperatures of 220°C–600°C. The ratio of FeF_3 in fluoridated film reaches up to 50% at 400°C as the fluoridation temperature rises.
The compound-phase composition and the crystal growth must be avoided in the passivation process because FeF$_3$ is converted to FeF$_2$ and affects the crystallinity of the film in the thermal modification process. It is confirmed that the optimum fluoridation temperature is lower than 320°C.

IV. OPTIMUM CONDITION FOR THERMAL MODIFICATION

A. Perfect Stoichiometric Structure

The direct fluoridated film contains excessive amount of fluorine in its lattices or interstices before the process of thermal modification. As described in the previous papers [6]-[8], it has a non-stoichiometric structure. Therefore, the direct fluoridated film does not have favorable characteristics in terms of the corrosion resistance, outgassing and other aspects. However, it is possible to convert the nonstoichiometric structure with the mole ratio of F/Fe = 2.27 to the stoichiometric structure with the mole ratio of F/Fe = 2.00 through the process of thermal modification. It is also obvious that most of the excessive fluorine diffuses to reach the interface between the fluoridated film and the stainless steel in the fluoridated film, at which the film is made thicker and has the stoichiometric structure after the thermal modification.

B. Surface Transition Change

Another characteristic of the thermal modification is the transition of chromium to the surface of the fluoridated film, where chromium is changed to a thin chromium fluoride film with the thickness of 100 Å or less on the FeF$_2$ film with the stoichiometric structure [6]-[8]. The chromium migration is also observed in the oxidation passivation at 400°C-500°C and in the thermal treatment of the stainless steel at 1000°C [13], [14]. In the case of fluoridation, however, the chromium transition is observed at the temperature of 400°C or lower due to the highest electronegativity of fluorine. Chromium fluoride has better corrosion resistance than iron fluoride.

C. Fluorine Evolution

A large amount of excess fluorine diffuses into the film, but a small amount of fluorine is released from the surface of fluoridated film in the process of thermal modification. The released fluorine from the film is measured.

A fluoridated tube with 1 m long and 1/4 inch diameter was filled with helium gas at the pressure level of 760 Torr at the room temperature. Then the tube was directly heated to 300°C or 400°C with the electric current controlled at 1 A for 1 hour [15]. After the temperature of tube returned to the room temperature, the released fluorine gas was measured by the gas chromatography, using helium as carrier gas. The same measurement was repeated until the released fluorine was not observed. The thermal modification was carried out for these films to confirm the difference of fluorine release time at the two different temperatures of 300°C and 400°C.

The results were shown in Figs. 5 and 6. In Fig. 5 the film formed at 200°C for 250 minutes has about two times film thickness compared with the film for 80 minutes. The fluorine release time were independent of the film thickness at the detection limit of gas chromatography of 1 ppm, when the thermal modification was carried out at 400°C for 3 hours.

On the contrary, at 300°C of the thermal modification, the fluorine evolution continued for 7 hours. The same results were obtained in Fig. 6. In order to form a perfect passivated film in terms of the fluorine evolution, thermal modification temperature is desirable to be higher than fluoridation temperature, that is, at 400°C and the thermal modification time must be set for 3 and more hours based on the above-mentioned results.

D. Chemical Composition Change and Crystallinity Control

The chemical composition change of the single phase FeF$_2$ formed at the fluoridation temperature of 220°C was examined at the thermal modification temperature of 320°C-500°C.

It has been confirmed from Fig. 7 that the chemical composition in the single film remains unchanged even when the temperature of thermal modification is raised to 500°C. Moreover, the crystal does not grow at temperatures below 400°C.

On the other hand, as shown in Fig. 8, a complicated
chemical composition change is observed when the compound film with FeF₂ and FeF₃ formed at 330°C or higher undergoes thermal modification. Figure 8 shows that, in the case of thermal modification at 400°C, FeF₃ peaks decrease, and that they completely disappear at 440°C. In the reductive ambient containing excessive amount of bare metals, FeF₃ is converted to FeF₂.

Pure iron plates were also selected to study the fluoridation of iron. Fig. 9 shows the XRD patterns after the fluoridation at 350°C and the thermal modification at 300°C-400°C. Just as observed for stainless steel, FeF₃ peaks decrease as the temperature of thermal modification rises and start to disappear at 400°C.

As shown in (b) of Fig. 10, the microcrystals and grain boundaries, which are trigger of corrosion, are observed in the fluoridated film formed at the high temperature. The crystal growth causes the cracks in the fluoridated film increasing with temperature and time of the thermal modification as shown in Fig. 11. This is the reason why the crystallinity of the fluoridated film in the process of thermal modification must be prevented.

Fig. 12 shows the relation between the interplanar spacing of FeF₂ and the temperatures of thermal modification. The film fluoridated at 220°C has wider interplanar spacing than the one fluoridated at 340°C. Although the gap between the two initial values is considerably wide, it gets smaller as the temperature tops 400°C, and the interplanar spacing values of two cases get closer to a certain level.

The relation between the crystallinity of passivated film
and the time of thermal modification at the temperature of 440°C are shown in Fig. 13. In Fig. 13, the interplanar spacing values sharply drop after a few hours of thermal modification. It is confirmed that the thermal modification temperature must be set under 400°C in order to prevent crystallinity.
V. Conclusion

The optimum conditions for the overall passivation technology were discussed, focusing on 316L stainless steel to expand the previously published methodology [6]. The surface roughness of the passivated film was also studied to find out the effect of the temperatures on the baking process followed by the fluoridation and passivation treatment. It has been found that the baking temperatures have a significant effect on the surface roughness of the passivated film. Consequently, the baking must be carried out at the same temperature level of the thermal modification or at higher levels.

The direct fluoridation products have the FeF$_2$ single-phase composition at the temperatures of 320°C or lower while they have the compound-phase composition with FeF$_3$ and FeF$_4$ when the temperature tops 330°C. FeF$_2$, in the compound-phase composition is converted to FeF$_3$ in the process of thermal modification to occur crystallinity. The microcrystals and grain boundaries are observed in the fluoridated film formed at the high temperatures. The phase conversion and the micro-crystallization, which lead to the cracks on the surface, are not desirable for the passivated film.

The thermal modification is very important process to form the perfect passivated film [6]. The optimum temperature of the thermal modification was examined in the case of the single-phase and the compound-phase composition with the evaluations of the fluorine evolution and the crystallinity.

The single-phase composition is more favorable for the passivation than the compound-phase composition. However, when the thermal modification is carried out at the temperature of 400°C or higher, the passivated film gets cracked accompanying the microcrystals even in the fluoridated film with the single-phase composition. The thermal modification must be carried out at the temperatures of 400°C or lower.

References

transfer in the multi-valleys, high field transport in semiconductor such as unified theory of space-charge dynamics in negative differential mobility materials, block oscillation induced negative mobility, and block oscillators, and dynamics in injection lasers. He is presently a Professor in the Department of Electronics, Faculty of Engineering, Tohoku University, where he is engaged in research on high performance ULSI such as ultra high speed ULSI, current overshoot transistor LSI, HBT LSI and SOI on metal substrate; base store image sensor (BASIS) and high speed flat panel display; and advanced semiconductor process technologies; i.e., ultra clean technologies such as high quality oxidation. Also, high quality metalization due to low kinetic energy particle bombardment; very low temperature Si epitaxy having simultaneous doping capability due to low kinetic energy particle bombardment; crystallinity control film growth technologies from single crystal; grain size controlled polysilicon and amorphous due to low kinetic energy particle bombardment; in situ wafer surface cleaning technologies due to low kinetic energy particle bombardment; highly selective CVD, and RIE. In addition, high quality ion implantations having low temperature annealing capability, etc.; based on the new concept supported by newly developed ultra clean gas supply system; ultra high vacuum compatible reaction chamber having self-cleaning function; ultra clean wafer surface cleaning technology, etc.

His research activities include 260 original papers and 190 patent applications. He received the Ichimura Award in 1979, the Teshima Award in 1987, and the Inoue Harushige Award in 1989. He serves as a General Chairman of the International Symposium on Power Semiconductor Devices and of the Institute of Basic Semiconductor Technology Development (Ultra Clean Society).

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