J. Soc. Cosmet. Scientists Korea
Vol. 34, No. 4, December 2008, 269-274

# 마이크로웨이브로 증폭된 습식 에칭에 의한 표면 개질 마이카의 제조와 특성

전 상 훈† · 권 순 상 · 김 덕 희 · 심 민 경 · 최 영 진 · 한 상 훈

아모레퍼시픽 기술연구원

(2008년 11월 24일 접수, 2008년 12월 11일 채택)

# Preparation and Characterization of Surface Modified Mica by Microwave-enhanced Wet Etching

Sang Hoon Jeon†, Sun Sang Kwon, Duck Hee Kim, Min Kyung Shim, Young Jin Choi, and Sang Hoon Han

R&D Center, AmorePacific Corporation, 314-1, Bora-dong, Kiheung-gu, Yongin-si, Gyunggi-do 449-729, Korea

(Received November 24, 2008; Accepted December 11, 2008)

요 약: 본 연구를 통해 반도체 산업에서 유래된 마이크로웨이브 증폭 에칭기술(MEE)을 이용하여, 마이카의 표면 구조를 변화시키고 오일 흡유량을 조절할 수 있었다. 마이크로웨이브 에너지가 마이카에 조사되면, 마이카 표면이 몇 분 이내에 에칭이 된다. 에칭의 결과로 마이카의 오일 흡유량이 증가되고, 마이카 $SiO_2$층의 표면 변화에 의해 백색도가 증가한다. 추가적으로, 땀을 흡수한 이후에도 높은 백색도가 유지된다. 마이카의 표면구조의 변화는 불산에 슬러리화된 마이카에 마이크로웨이브 조사를 통해서 이루어졌다. 에칭의 정도는 산의 농도, 조사 시간, 조사 에너지의 양, 슬러리의 농도에 의해 조절되었다. 에칭된 마이카의 표면 구조는 '달' 표면 모양과 유사하게 보인다. 표면적과 거칠기 등의 특성은 Brunauer-Emmett-Teller (BET), atomic force microscopy (AFM), scanning electron microscopy (SEM), Spectrophotometer, goniophometer로 측정되었다.

**Abstract:** In this study we successfully altered the structural characteristics of the mica surface and were able to control oil-absorption by using the microwave enhanced etching (MEE) technique, which has originally been used in semiconductor industry. When microwave energy is applied to the mica, the surface of the mica is etched in a few minutes. As the result of etching, oil-absorption of the mica was enhanced and surface whiteness was improved by modifying the silicon dioxide layer. Additionally, the high whiteness was maintained even though the etched mica absorbed the sebum or sweat. The surface modification of mica was performed by microwave irradiation after the treatment of hydrofluoric acid. The degree of etching was regulated by acid concentration, irradiation time, the amount of energy and slurry concentration. The surface morphology of the etched mica appears to be the shape of the 'Moon'. The characteristics of surface area and roughness were examined by Brunauer-Emmett-Teller (BET) surface area analysis, atomic force microscopy (AFM), scanning electron microscopy (SEM), spectrophotometer and goniophotometer.

***Keywords:*** *microwave enhanced etching, surface modification, oil-absorption, mica, cosmetics*

## 1. Introduction

To adjust the skin color tone, we combined talc, $TiO_2$, and $Fe_2O_3$, the cosmetic raw materials that contain highly refractive pigments. However, the problem with these materials as a high covering powder is that they tend to make the makeup thick, make hair follicles visible to the eye and yet have low skin transparency, and leave an unnatural finish. These inorganic pigments are also in trouble because they originally have low brightness or saturation. When they are wet in water or sebum, the brightness and saturation are reduced

† 주 저자 (e-mail: shjeon@amorepacific.com)

even further to make the makeup film dark thus spoil the makeup effects.

Meanwhile, the beauty of skin appearance is greatly influenced by skin denseness. If the skin becomes denser, light is more uniformly reflected from the skin, increasing the transparency of the skin. Thus, a transparent, flake-like powder having excellent adhesion to the skin is preferred to the conventional materials that take advantage of the covering action caused by a light scattering effect.

To use the pure transparency of synthetic mica among inorganic pigments as well as the characteristics of the scale-like smooth surface of the synthetic mica, attempts were made to develop new products that have high particle uniformity with high aspect ratio and to produce a cosmetic raw material that has good gloss or transparency to present a dense skin.

However, such transparency or gloss imposes limitations on the use of mica in pact formulations. The scale-like smooth surface of mica tends to present glossiness instead of giving transparency, showing darkness caused by a change in color after the make-up application, thus reducing the make-up lasting properties. Thus, the use of mica in pact formulations has limitation, unlike other formulations. Moreover, mica has a low ability to absorb sebum, and becomes wet easily even in a small amount of sebum that the color thereof becomes dark. This is a common problem in plate-like inorganic pigments.

In an actual make-up film, the secretion of sweat is also a problem. In a high-temperature and high-humidity condition in the rainy or summer season, in which a large amount of sweat is secreted, sebum and sweat interact with each other. When the amount of sebum in a make-up film is excessive, the make-up film is separated and floats on the surface while it is admixed with sebum. In addition, a large amount of sweat was observed to flow and push the flowable makeup film, thus promoting the breakdown of the make-up.

To increase the sebum-absorbing capability of mica, the method of coating mica with a surface-treating substance such as dimethicone or triethoxycarprylylsilane, has been used, but it is not easy to solve the problems associated with the inherent glossiness of mica. Thus, mica materials with a relatively low glossiness have been used, but they too have encountered limitations. However, no method has yet been developed for solving the glossiness of mica materials while maintaining the sensory feel thereof.

Transparency and glossiness, the typical characteristics of mica, are not suitable for the base make-up cosmetics. The surface of mica tends to be glossy by a reflection of light. When it is applied to the face, it often absorbs sebum and sweat and tends to appear a dark and dull color. For these reasons, use of the mica has in fact been limited in makeup cosmetics compared with other inorganic components. Furthermore, mica is easily wetted even with a small amount of sebum and sweat because of its low capacity of oil-absorption. As a result, the color of mica becomes dark and dull.

The etching process is used in numerous industrial applications. For example the energy released by the alpha decay is transformed partly into a so-called alpha-recoil track (ART)[1-3]. The track can be enlarged by treating the mica with an appropriate etchant (e.g. HF).

Our study focuses on the application of microwave enhanced etching[4,5], which has been used in semiconductor industry, to alter the surface morphology of synthetic mica and eventually to control the oil-absorption capacity and the optical characteristics of luster and whiteness.

The changes in the microstructure and physical properties of the etched mica obtained are investigated by using Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM)[6,7], atomic force microscopy (AFM)[8-10], spectrophotometer, goniophotometer and ASTM D281-95 standard method[11].

## 2. Materials and Methods

### 2.1. Sample Preparation

The pretreatment process of fluoro-mica powder is as follows:

The fluoro-mica with an average size of 12 $\mu$m

**Table 1.** Oil-absorption and Whiteness of Fluoro-mica Before and After Microwave Etching Process

| Sample | Oil-absorbtion (cc/g) | Whiteness (L*) |
|---|---|---|
| *N*-fluoro-mica | 0.432 ± 0.023 | 86.5 ± 0.31 |
| *E*-fluoro-mica | 0.735 ± 0.038 | 93.2 ± 0.28 |

(received from CO-OP chemical Inc., Japan) was used. 10 g of fluoro-mica was added into 90 g of 2 % aqueous hydrofluoric acid solution (10 wt% slurry). The mixture solution was put into a microwave reactor (Daewoo Electronics, W = 620 watts, frequency = 2.45 GHz), and then heated under microwave irradiation at atmospheric pressure for 60 ~ 300 s. To investigate the effects of microwave-enhanced etching, the remaining procedures were also carried out for the same material without the etching process. The fluoro-mica with etching and that without etching are denoted as *E*-fluoro-mica and *N*-fluoro-mica, respectively (*E* means the etched sample and *N* means the non-etched sample). The resulting mixture was pulverized on a grinding instrument after washing, filtering and drying. The degree of etching was influenced by acid concentration, irradiated time, the amount of energy and slurry concentration.

### 2.2. Characterization

SEM images were collected on a Hitachi S-4300 (Hitachi Co., Ltd., Japan) operating at 1.00 kV. The elemental compositions of the samples were determined by using energy dispersive X-ray (EDX) analysis at 20.0 kV attached on the SEM instrument.

The surface areas were obtained by applying the BET treatment in the domain of relative pressures 0.05 ~ 0.25, and also by the Langmuir method for the pillared forms. The total pore volume was determined from the amount of nitrogen absorbed at a relative pressure of 0.985, whereas the *t*-plot method[12] was used to obtain the micro pore volume.

The particle size distribution of the mica samples collected at the different condition was determined on a Coulter LS-130 instrument. The results are expressed as percentages of volume of the particles versus their equivalent average radius.

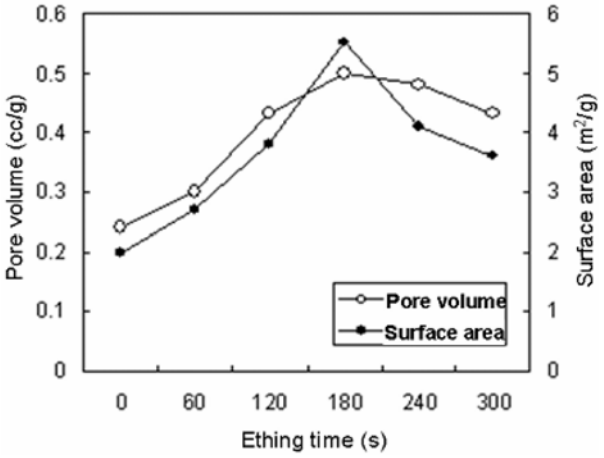


**Figure 1.** The change of BET pore volume and surface area of the *E*-fluoro-mica as a function of the microwave etching time.

The solution (approximately 0.1 mL) of the dispersed particles was deposited on carbon tape, then oven-dried at 100 ℃ for 1 h. The preprocessed samples were analyzed in the AFM equipment after temperature equilibration. The solution was diluted until individual or separate particles could be seen in the AFM images. Room temperature and air humidity were kept at around 24 ℃ and lower than 50 %, respectively. The samples were prepared using the previously described procedure and each sample was imaged at two different positions.

The gonio-photometer is based on polarized reflectance at continuous angles, and the changes in polarized phase are used in combination to determine the optical properties of surfaces. The gonio-photometer generally measures the intensity and phase around the Brewster angle at which position the reflected intensity of light polarized parallel to the incident plane is zero for a smooth surface. The phase of the polarized light also goes through an 180° change at this angle. Changes in the surface (due to molecular layers, particles or surface roughness) influence the measurable values of the continuous angle. These values determine the optical properties of the surface layer.

## 3. Results and Discussion

Figure 1 shows the variations in BET surface of mica

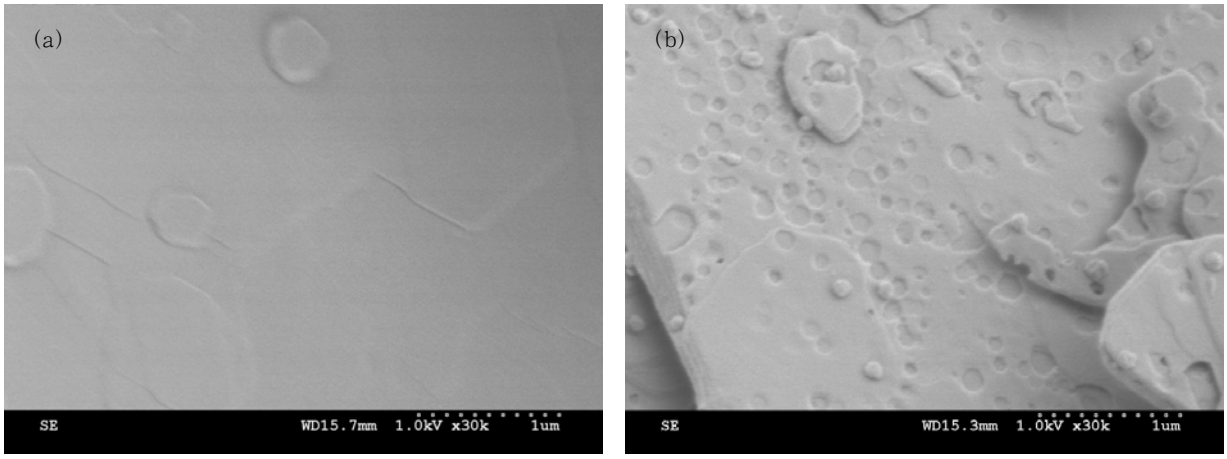


**Figure 2.** SEM of mica surfaces: (a) *N*-fluoro-mica, (b) *E*-fluoro-mica.

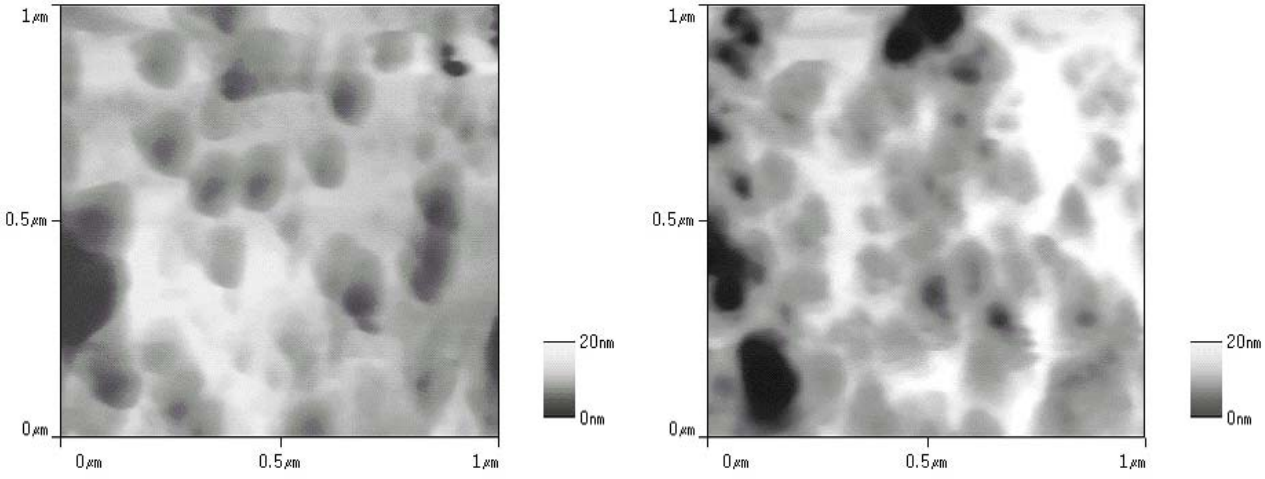


**Figure 3.** AFM images of highly concentrated holes at two different positions.

that occurred with the irradiation time of microwave in the etching process. When the mica sample was etched for 180 s under microwave irradiation, the surface area increased up to three times than that of the non-etching mica. However, the SEM image made a little difference between the surface of mica before and after the microwave etching process, as shown in Figure 2. The increase in the surface area means that the microwave etching process enhances nano-roughness of the mica surface. The surface areas reach the maximum at 180 s and decrease again to less than 3.6 $m^2/g$, which indicates the formation of very smooth surfaces. In addition, the total pore volumes reach the maximum at 180 s, and they gradually decrease. It is reasonable to infer that the nano-roughness induced by the etching process plays an important role in the physical property of mica. *E*-Fluoro-mica sample refers to the sample obtained by microwave-enhanced etching process for 180 s.

Figure 3 shows the height and friction images of the 1 $\mu m^2$ area obtained in a single particle. It shows AFM images of the highly concentrated holes at two different position. After scanning a 1 $\mu m^2$ area, an image of the fluoro-mica surface was captured. The holes appeared on the surface when microwave enhanced etching was applied. Some holes that had the shape of the 'Moon' (approximately 50 to 150 nm size) were observed in AFM images. The intensities of images in the gray scale of other holes are lower than the bare

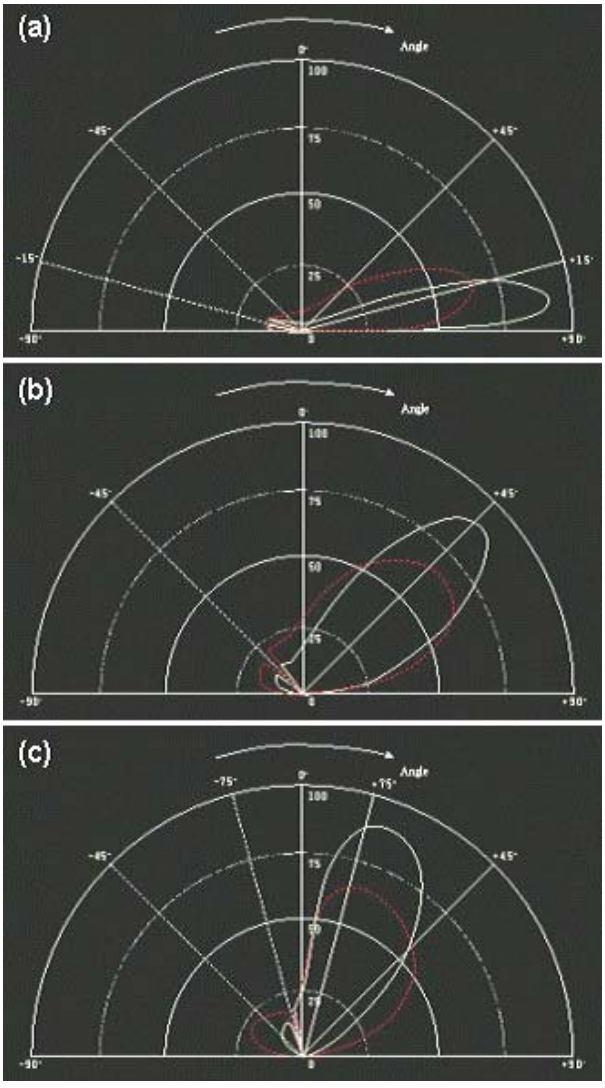


**Figure 4.** Reflectivity curves of goniophotometer at (a) 15°, (b) 45°, (c) 75°: (a dotted line) *N*-fluoro-mica, (a full line) *E*-fluoro-mica.

surface. The measured depth of the holes is between 7 and 15 nm.

The gloss of fluoro-mica is the shiny appearance perceived on the surface. We quantified the gloss with goniophotometer that measures the multi-directional reflectance for incident angles from 0 to 180°. We measured the reflectance of incidence angles at 15°, 45° and 75° (Figure 4). The specular reflection is decreased over 20 %, and it can be recognized as the soft-focus effect by diffused reflection. The reflection is comprised of a scattered and specular component. The light is dispersed in all directions as it decreased in specular reflection. A scattered component is one that light is reflected through all angles. The surface modification of *E*-fluoro-mica indicates that there is a soft-focus effect by scattered reflection. The soft-focus effect is the ability of *E*-fluoro-mica to reduce the visible signs of fine lines. Such an effect is achieved optically by the interaction of visible light with *E*-fluoro-mica particles.

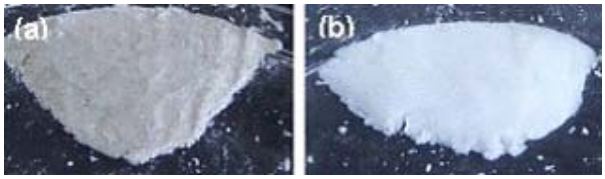


**Figure 5.** The whiteness of oil-absorbed mica: (a) *N*-fluoro-mica, (b) *E*-fluoro-mica.

We measured the oil-absorption in compliance with the American Society for Testing and Materials (ASTM) D281-95 standard method. When the fluoro-mica sample is etched by microwave irradiation, the oil-absorption increases up to over 170 % per gram. Also, the luster of fluoro-mica have been examined by Glossmeter. The refractive values decreased on the mica surface after microwave enhanced etching. Oil-absorption was influenced by the surface area, pore volume and mass volume-density. Mass volume-density increased about 150 % by microwave enhanced etching (data not shown).

When the fluoro-mica sample is etched by microwave irradiation, the whiteness of oil-absorbed mica was improved (Figure 5). The L* value of spectrophotometer represents the whiteness of powder. The range of L* value is 0 to 100. If L* value is $\Delta L = 1$, the value is recognized as different colors.

## 4. Conclusion

The alpha-recoil track was enlarged by treating the mica with an appropriate etchant (e.g. HF). We applied microwave enhanced etching technique to alter the surface of inorganic particle and were able to control oil-absorption, luster and whiteness. By using microwave energy and etching inorganic particles on the surface, oil-absorption was increased, and whiteness

was improved on the silicon dioxide layer. The degree of etching was influenced by acid concentration, irradiated time, the amount of energy and slurry concentration until the surface area of mica increased with a 'shape of the Moon'. The width and depth of etched holes were controlled to a fixed quantity with atomic force microscope. The result of the goniophotometer measurement revealed that the specular reflection decreased over 20 %, and the soft-focus effect was identified by diffused reflection. The oil-absorption increased up to over 170 % per gram. We applied microwave enhanced etching to the cosmetic industry for the first time to solve the fundamental problems associated with high luster, low oil absorption, and whiteness. Our application of fluoro-mica not only improved the whiteness but also reduced the gloss significantly.

## References


1. R. L. Fleischer, P. B. Price, and R. M. Walker, Nuclear tracks in solids, University of California, Berkeley, CA (1975).
2. S. A. Durrani and R. K. Bull, Solid state nuclear track detection, Pergamon, Oxford (1987).
3. R. Spohr, Ion tracks and microtechnology: principles and applications, Vieweg, Braunschweig (1990).
4. S. J. Pearton, F. Ren, and C. R. Abernathy, Enhanced etch rates of tri-level resist stacks in microwave discharges, *Semicond. Sci. Technol.*, **8**, 1905 (1993).
5. M. Kang, J. M. Kim, J. W. Kim, Y. K. Kim, H. Chung, and J. E. Yie, Simple and fast microwave-enhanced wet etching of SiC particles for electroless Ni-P platin, *Surface and Coating Technology*, **161**, 79 (2002).
6. L. A. Bursill and G. Braunshausen, Heavy-ion irradiation tracks in zircon, *Phil. Mag.*, **A62**, 395 (1990).
7. R. Scholz, J. Vetter, and S. Hopfe, Observation of latent heavy-ion tracks in GeS by transmission electron microscopy, *Rad. Eff. Def. Solids*, **126**, 275 (1993).
8. F. Thibaudau, J. Cousty, E. Balanzat, and S. Bouffard, Atomic-force-microscopy observations of tracks induced by swift Kr ions in mica, *Phys. Rev. Lett.*, **67**, 1582 (1991).
9. S. Bouffard, Y. Pennec, J. Cousty, and F. Thibaudau, Swife heavy ions in matter conferences: SHIM 92, *Rad. Eff. Def. Solids*, **126**, 225 (1993).
10. J. Ackermann, N. Angert, S. Grafstrom, M. Neitzert, R. Neumann, C. Trautmann, and J. Vetter, Scanning force microscopy of heavy-ion tracks, *Radiat. Eff. Def. Solids*, **126**, 213 (1993).
11. Standard practice for goniophotometry of objects and materials, ASTM E 167, American Society for Testing and Materials, West Conshohocken, PA (1995).
12. J. C. P. Broekhoff and J. H. de Boer, Studies on pore systems in catalysts: XIV. Calculation of the cumulative distribution functions for slit-shaped pores from the desorption branch of a nitrogen sorption isotherm, *J. Catal.*, **10**, 391 (1968).