Superhydrophobic property of the perpendicular nanosheet film by hot water treatment of the metal aluminum

Eiji HOSONO, Yarong WANG, Masaki ICHIHARA* and Haoshen ZHOU†

National Institute of Advanced Industrial Science and Technology, 1-1-1, Umezono, Tsukuba 305-8568

*Material Design and Characterization Laboratory, Institute for Solid State Physics, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8581

The superhydrophobic property attracts many researchers in the both field of academe and industry. All of the superhydrophobic materials have the rough surface structure based on the Cassie-Baxter equation. The trapping of air into the rough surface structure caused the improvement of the superhydrophobic property. Therefore, the nanostructure control technique is very important. Of course, considering application in industry, the process cost of the superhydrophobic materials is very important. In this work, the superhydrophobic film is fabricated by the hot water treatment, which is one of the chemical bath deposition methods, of the metal aluminum. The hot water process of sputtered Al film on the glass substrate results in the fabrication of the high transparent superhydrophilic film constructed by perpendicular nanosheet structure. After fluoroalkylsilanes coating, the resultant film shows the high transparent superhydrophobic property. Moreover, these processes can be applied to the commercial Al foil. So, we can easily obtain superhydrophobic film by using the hot water process.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Nanosheet, Superhydrophobicity, Superhydrophilicity, Chemical bath deposition

[Received November 10, 2008; Accepted January 15, 2009]

1. Introduction

The superhydrophobic property attracts many researchers in the both field of academe and industry.¹⁾⁻⁹⁾ Especially, in these days, the industrial needs of superhydrophobic materials are increased. Today, we face the environmental and resource problems and need energy-saving system. So, the development of the superhydrophobic materials are very important because the superhydrophobic film can be applied to not only anti-wetting for window, but also electrode of fuel cell,¹⁰⁾ anti-snow (or ice)-adherence¹¹⁾ on power transmission lines and wing of air plane.

All of the superhydrophobic materials with a contact angle of over 150°, have the rough surface structure based on the Cassie-Baxter equation.¹²⁾ The trapping of air into the rough surface structure caused the improvement of the superhydrophobic property. Of course, for application in industry, the process cost of the superhydrophobic materials is very important. Although the nanostructure control of the surface is very important for the superhydrophobic property, the nanostructure control of the surface by top down process or bottom up process using vacuum system is high cost process. The bottom up process such as the chemical bath deposition (CBD)¹³⁾ is very low cost and low environmental load process. CBD processes can be used to easily obtain many kinds of nanostructure including nanosheet,¹⁴⁾⁻²²⁾ nanorod,^{8),23)-25)} and nanopin.^{4),26)} So, the CBD process is suitable for nanostructural control of the superhydrophobic materials. In the CBD method, there are three kinds of starting precursor solutions. One is a using of the solution including the metal ion due to the dissolving of the metal salts and so on.^{14)-17),19)} After the reaction of the metal ion solution, metal compounds are deposited on the substrate. Second process is the using the solution immersed solid materials as the source of metal ions.²⁰⁾⁻²²⁾ At

first, the solid materials are dissolved into the solution. After that, redeposition caused the deposition of the metal compounds on the substrate. When the solubility is low and the supersaturation ratio is high, the fabrication of the precursor solution is difficult. In that case, the latter process is suitable.²²⁾ Third process is used both solid materials and metal salts solution.¹⁸⁾

Tadanaga et al. reported the transparent superhydrophilic or superhydrophobic film based on flower-like Al₂O₃, which is obtained by the hot water treatment of the sol-gel derived Al₂O₃ gel film.^{2),20)} In spite of very simple and low cost process, the superhydrophilic or superhydrophobic property are very high. In this work, we used the metal aluminum as the source of the nanosheet films. When the Al sputtered glass film was immersed into the hot water, the transparent film constructed by the perpendicular nanosheet was obtained. After hydrolyzed fluoroalkylsilanes (FAS) coating, the film indicate good superhydrophobic property. Moreover, we can obtain superhydrophobic film by using commercial Al foil as well as sputtered Al film. Because Al metal is applied to various uses, moreover, easy and direct construction of the superhydrophobic surface on the Al metal surface is very useful technique.

2. Experimental

The sputtering of Al is conducted by the Sibaura CFS-4EP-LL. The thickness of the Al film on the glass substrate is around 70 nm. The sputtered Al film or commercial Al foil are immersed into the hot water at 90°C for 90 min. After washing and drying of those films, the films were immersed into the hexane with 1 vol% of heptadecafluorodecyltrimethoxysilane, which is one of the FAS, at 60°C for 5 h.

3. Results and discussion

Figures 1(a) and (b) shows the SEM images of the surface after the hot water treatment of sputtered Al film and commercial

† Corresponding author: H. Zhou; E-mail: hs.zhou@aist.go.jp

Fig. 1. SEM images of the surface after the hot water treatment of sputtered Al film on the glass substrate (a, c) and commercial Al foil (b) at 90°C for 90 min.

Fig. 2. (a) TEM image of the nanosheet, which is fabricated by the hot water treatment of sputtered Al film on the glass substrate at 90°C for 90 min. (b) The electron diffraction pattern of the nanosheets.

Al foil at 90°C for 90 min, respectively. From both images, we can see the perpendicular nanosheet structure. So, the nanosheet structure, which is fabricated by the hot water treatment of Al_2O_3 gel film,^{2),20)} could be obtained by using metal Al film, too. The cross-section image (Fig. 1(c)) of the nanosheet film obtained from sputtered Al film shows the film thickness of around 600 nm. The TEM image of the nanosheet, which is obtained from sputtered Al film, is shown in Fig. 2(a). The very thin nanosheets with thickness of several nm are easily obtained. Figure 2(b) is the electron diffraction pattern of the film after hot water treatment of the sputtered Al film. We can not identify the nanosheet from this electron diffraction pattern because this indistinctly rings indicate that the nanosheet is amorphous. When we observed the nanosheet at high resolution condition, we could rarely see the lattice fringe. However, almost of those nanosheets were amorphous.

Figure 3 shows the transmittance of the normal glass substrate (a), the glass substrate with the nanosheets by the hot water treatment of the sputtered Al film (b), and the glass substrate with the nanosheet coated by FAS (c), respectively. The transmittance of the glass substrate with the nanosheet in Fig. 3(b) shows the higher transmittance than that of the normal glass substrate in Fig. 3(a). At the wavelength of 500 nm, the nanosheet film indicates the improvement of the transmittance of 3%. Of course, the high transmittance of the nanosheet films is maintained after the FAS coating as shown in Fig. 3(c). It is considered that these

Fig. 3. Transmittance of the various glasses. (a) normal glass substrate, (b) the glass substrate with the nanosheets by the hot water treatment of the sputtered Al film, and (c) the glass substrate with the nanosheet coated by FAS.

Fig. 4. Wettability of the nanosheet films by the hot water treatment of the sputtered Al film.

antireflective effects are due to the reflective index gradient by the specific structure.²⁷⁾

We checked the wettability property of the nanosheet films. Figure 4 shows the superhydrophilic property of the nanosheet films by the hot water treatment of the sputtered Al film. The water drop is immediately spread on the surface. It is called as superhydrophobic property and it is based on the Wenzel model. Wenzel equation is indicated as Eq. (1).²⁸⁾

$$\cos \theta' = r \cos \theta \quad (1)$$

θ , θ' and r are the contact angle of a liquid on the flat surface, superficial contact angle on the rough surface, and roughness factor of the surface, respectively. This model means that the surface roughness enhances both the hydrophilic property of the hydrophilic surface and the hydrophobic property of the hydrophobic surface. The specific structure of nanosheet film caused the superhydrophilicity based on the Wenzel mode.

Figures 5(a) and (b) show the superhydrophobic property of the FAS coated nanosheet films on the glass substrate by the hot water treatment of the sputtered Al film and FAS coated nanosheet films on the commercial Al foil, respectively. The high contact angle of over 160° is confirmed from both images. This superhydrophobic property is based on the Cassie–Baxter model. The Cassie–Baxter equation is indicated as Eq. (2).¹²⁾

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2)$$

θ_c , θ_1 and θ_2 are the superficial contact angle, contact angles of flat films of components 1 and 2, respectively; and f_1 and f_2 are surface area fractions of components 1 and 2, respectively. If component 2 is the air with a water CA of 180° , the Eq. (2) is indicated as Eq. (3).

Fig. 5. Superhydrophobic property of the FAS coated nanosheet films on the glass substrate by the hot water treatment of the spattered Al film (a) and FAS coated nanosheet films on the commercial Al foil (b).

Fig. 6. Images of the film with the perpendicular nanosheets on the glass substrate (a), the film with the perpendicular nanosheets/glass substrate coated by FAS (b) and the film with the perpendicular nanosheet coated by FAS on the commercial Al foil (c).

$$\cos\theta_c = f_1(\cos\theta_1 + 1) - 1 \quad (3)$$

This equation means that films with the small f_1 and the large θ_1 indicate superhydrophobic property. The specific nanostructured film is constructed by the perpendicular nanosheets with the thickness of several nm. So, the value of f_1 is very small. The value of θ_1 is high due to the coating of FAS. The resultant film shows the good superhydrophobic property.

Finally, Fig. 6 shows the images of the film with the perpendicular nanosheets on the glass substrate (a), the film with the perpendicular nanosheets/glass substrate coated by FAS (b) and the film with the perpendicular nanosheet coated by FAS on the commercial Al foil (c). The images of (a) and (b) indicate good transparency. And the images of (b) and (c) shows the good superhydrophobicity. The easy fabrication of the nanosheet structure on the commercial Al foil by only the hot water treatment is very useful because the nanosheet morphology, which is suitable for superhydrophobic and superhydrophilic property, is easily obtained on not only the flat Al foil but also the Al surface with complicated morphology.

4. Summary

The perpendicular nanosheet film is easily obtained from the metal aluminum by using hot water treatment. From the spattered Al film on the glass substrate, the high transparent superhydrophilic film is fabricated. After FAS coating, the resultant film shows the high transparent superhydrophobic property. Because these simple processes can be applied to the commercial Al foil, we can easily obtained superhydrophobic film by using

the hot water process, which is one of the chemical bath deposition methods.

References

- 1) T. Onda, S. Shibuichi, N. Satoh and K. Tsujii, *Langmuir*, **12**, 2125–2127 (1996).
- 2) K. Tadanaga, N. Katata and T. Minami, *J. Am. Ceram. Soc.*, **80**, 1040–1042 (1997).
- 3) K. Tadanaga, J. Morinaga, A. Matsuda and T. Minami, *Chem. Mater.*, **12**, 590–592 (2000).
- 4) H. Yabu, M. Takebayashi, M. Tanaka and M. Shimomura, *Langmuir*, **21**, 3235–3237 (2005).
- 5) E. Hosono, S. Fujihara, I. Honma and H. Zhou, *J. Am. Chem. Soc.*, **127**, 13458–123459 (2005).
- 6) X. Feng, J. Zhai and L. Jiang, *Angew. Chem. Int. Edn*, **44**, 5115–5118 (2005).
- 7) N. Yoshida, Y. Abe, H. Shigeta, A. Nakajima, H. Ohsaki, K. Hashimoto and T. Watanabe, *J. Am. Chem. Soc.*, **128**, 743–747 (2006).
- 8) L. C. Gao and T. J. McCarthy, *J. Am. Chem. Soc.*, **128**, 9052–9053 (2006).
- 9) E. Hosono, M. Ichihara and H. Zhou, *Nanotechnology*, **19**, 395605 (2008).
- 10) A. Nakajima, *J. Ceram. Soc. Japan*, **112**, 533–540 (2004).
- 11) W. Z. Li, X. Wang, Z. W. Chen, M. Waje and Y. S. Yan, *Langmuir*, **21**, 9386–9389 (2005).
- 12) A. B. D. Cassie and S. Baxter, *Trans. Faraday. Soc.*, **40**, 546–561 (1944).
- 13) B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxell, G. L. Graff, L. Song, J. Liu, J. W. Virden and G. L. McVay, *Science*, **264**, 48–55 (1994).
- 14) E. Hosono, S. Fujihara, T. Kimura and H. Imai, *J. Colloid Interf. Sci.*, **272**, 391–398 (2004).
- 15) E. Hosono, S. Fujihara, I. Honma and H. Zhou, *Adv. Mater.*, **17**, 2091–2094 (2005).
- 16) E. Hosono, S. Fujihara, I. Honma, M. Ichihara and H. Zhou, *J. Electrochem. Soc.*, **153**, A1273–A1278 (2006).
- 17) E. Hosono, S. Fujihara and T. Kimura, *Langmuir*, **20**, 3769–3774 (2004).
- 18) Y. F. Gao, M. Nagai, Y. Masuda, F. Sato, W. S. Seo and K. Koumoto, *Langmuir*, **22**, 3521–3527 (2006).
- 19) H. Ohgi, T. Maeda, E. Hosono, S. Fujihara and H. Imai, *Cryst. Growth Des.*, **5**, 1079–1083 (2005).
- 20) K. Tadanaga, N. Katata and T. Minami, *J. Am. Ceram. Soc.*, **80**, 3213–3216 (1997).
- 21) N. Yamaguchi, T. Nakamura, K. Tadanaga, A. Matsuda, T. Minami and M. Tatsumisago, *Crystal Growth & Design*, **6**, 1726–1729 (2006).
- 22) E. Hosono, H. Matsuda, I. Honma, M. Ichihara and H. Zhou, *Langmuir*, **23**, 7447–7450 (2007).
- 23) S. Yamabi, J. Yahiro, S. Iwai and H. Imai, *Thin Solid Films*, **489**, 23–30 (2005).
- 24) X. Hu, Y. Masuda, T. Ohji and K. Kato, *J. Colloid Interf. Sci.*, **325**, 459–463 (2008).
- 25) E. Hosono, S. Fujihara, K. Kakiuchi and H. Imai, *J. Am. Chem. Soc.*, **126**, 7790–7791 (2004).
- 26) E. Hosono, S. Fujihara, H. Imai, M. Ichihara and H. Zhou, *ACS Nano*, **1**, 273–278 (2007).
- 27) N. Yamaguchi, K. Tadanaga, A. Matsuda, T. Minami and M. Tatsumisago, *Thin Solid Films*, **515**, 3914–3917 (2007).
- 28) R. N. Wenzel, *J. Phys. Colloid Chem.*, **53**, 1466–1467 (1949).