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Impurity-Dependent Nanoporous Structures of Anodic Aluminum Oxides†

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With one-step anodizing, the highly nanoporous structures of anodic aluminum oxide were produced. The nanoporous structures were selectively formed in the combinatorial anodizing: (1) the low-purity aluminum and (2) phosphoric acid. The anodic aluminum oxide has unique structure with sprout-like surface, the main nanopores (180-210 nm) and the sub-nanopores at the bottom of main nanopores. This structure is explained by impurity model.

Keywords: Anodic aluminum oxide, Nanopore, Anodizing.

INTRODUCTION

Alumina nanopore arrays have attracted much attention due to various applications such as a perpendicular magnetic recording[1-3], photonic devices[4], catalysts[5] and as a substrate for carbon nanotube devices[6]. Masuda's pioneering work on two-step anodizing opened a new door to obtain ordered nanopore arrays in aluminum by stripping away the oxide layer obtained during a first anodizing step and by subsequently re-anodizing it[7-11]. Masuda *et al.* also developed a nanoindentation technique to get a pre-texturing of aluminum by imprinting with a SiC mold[12-14]. Recently, multi-step anodizing methods have been used to obtain a well ordered and size controlled pore channel in alumina[4,11]. Suh *et al.* have reported a new design method for control of nanohole shape. They fabricated a long funnel-like alumina tube using a voltage dropping from 40-20 V by 5 V steps for second anodizing[11]. Another issue in the anodic aluminum oxide (AAO) is the size reducing less than 20-30 nm because of super sensitive sensors, specific chemical reactor including catalytic reaction and controllability of photonic band[1-10]. However, the theoretical and experimental reports have revealed that the self-assembly limit of the pore size is around 20-30 nm due to low stress between nanopores[7-9].

In this study, we suggest a fabrication of highly porous structures, different from a variety of conventional anodic aluminum oxide structures made by anodizing methods of size reducing, shape control, length control and position control of pores. The highly porous structures can be obtained by a simple process of the one-step anodizing of low-purity Al under phosphoric acid solution.

EXPERIMENTAL

Anodic aluminum oxides were prepared *via* a one-step or two-step anodizing process. Two types of aluminum substrate were used: (1) high-purity Al (99.999 %) and (2) low-purity (general grade) Al (99.5 %). The Al substrates were degreased and electrochemically polished in a mixed solution of perchloric acid and ethanol (1:4 volume ratio) for 3 min at a constant current of 100 mA/cm^2 and a temperature below 1-2 ºC. The two-step anodizing was conducted for the high purity Al. The first anodizing of was conducted for 24 h at 20 ºC in a 0.3 M oxalic acid solution and then removed using a mixed solution of phosphoric acid (6 wt %) and chromic acid (1.8 wt %). The regular hexagonal nanohole arrays were prepared after the second anodizing for 10 min at 2 ºC. The one-step anodizing was conducted for both of high purity and low purity Al under oxalic acid and phosphoric acid. The obtained anodic aluminum oxide were characterized by a field emission scanning electron microscope (FE-SEM: JEOUL, JSM 6700F).

RESULTS AND DISCUSSION

Fig. 1(a) shows the FE-SEM image for the top view of anodic aluminum oxide after two-step anodizing for the high-purity Al. Size of the nanopore is 70-80 nm. Fig. 1(b) is the image of bottom structure after removing anodic aluminum oxide of Fig. 1(a). Fig. 1(a) and (b) indicate that nanopores at the top of anodic aluminum oxide have regular structure (self-

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assembled hexagonal-packed structure) and are stretched to the bottom of anodic aluminum oxide.

Fig. 1(c) and (d) are the images of anodic aluminum oxide after one-step anodizing for the low-purity Al under oxalic acid. The pore shape is very irregular, which is different from one-step anodizing for the high-purity aluminium. In general, although the regular structure between nanopores after one-step anodizing of high-purity Al are not formed, the size and shape of nanopores are similar to each other[12-14]. Importantly, a simple change in the condition of solution and purity of Al results in the dramatic change in porosity and pore shape. As shown in Fig. 2, the highly porous structure of anodic aluminum oxide is produced in the condition of one-step anodizing of low-purity Al under phosphoric acid (anodizing condition of 130 V for 2 h). The surface of anodic aluminum oxide has sprout-like structures as shown in Fig. 2(a) (see red-dotted circle). Main nanopore sizes are 180-210 nm (Fig. 2(c)) and sub-nanpores at the bottom of the main nanopores are also observed [Fig. 2(a)].

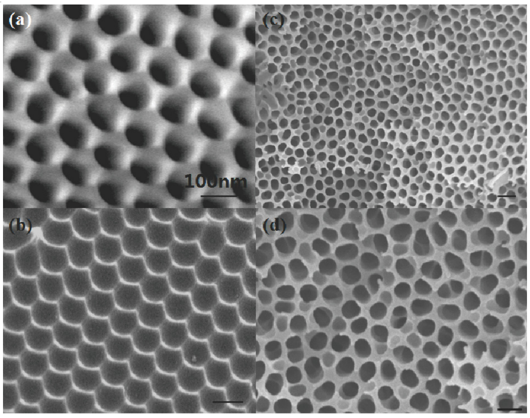

Fig. 1. Top (a) and bottom (b) FE-SEM image of anodic aluminum oxide after two-step anodizing for the high-purity Al. FE-SEM image after one-step anodizing for the low-purity Al (c and d). Oxalic acid is used as an anodizing solution

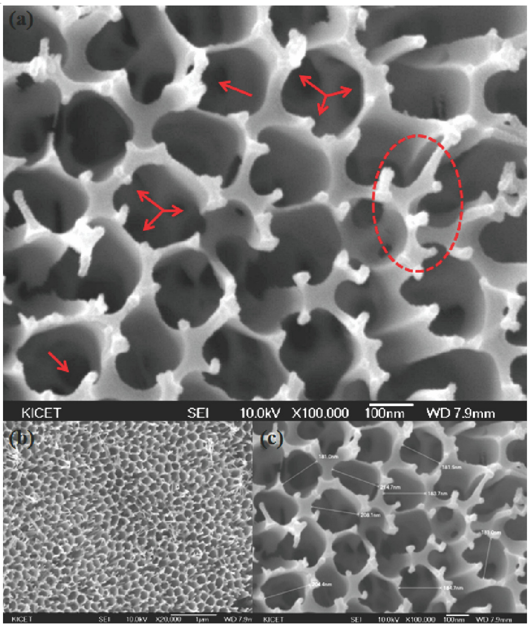

Fig. 2. FE-SEM images of anodic aluminum oxide after one-step anodizing for the low-purity Al in the condition of phosphoric acid

The structure of nanopores with sprout-like structures and sub-nanopores can be explained by impurity model as shown in Fig. 3. Anodizing path for the high-purity Al can be stretched to the bottom area due to no hindrances such as impurities or cavities (Fig. 3(a)). If there are many impurities of Al (this experiment: 0.5 %), anodizing path may be changed at the impurity areas and be randomly branched to the bottom areas (Fig. 3(b)). Furthermore, phosphoric acid play a role for the interlayer thinning between nanopores and partial surface resolving as explained by experimental section (resolving reagent for the anodic aluminum oxide).

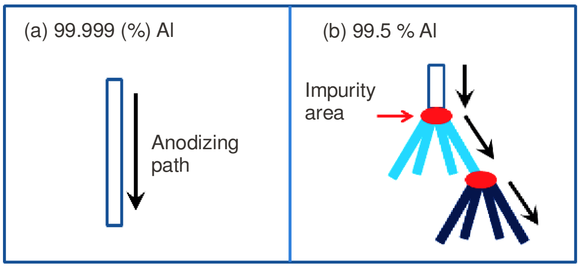

Fig. 3. Impurity model during one-step anodizing for low purity Al

Conclusion

Both of impurity of Al and phosphoric acid can play an important role for the producing of highly porous anodic aluminum oxide with main nanopores, sub-nanopores and sprout-like structures. The simple one-step anodizing method coupled with low-cost Al may help us study for porosity-dependent sensors, catalysts and optics.

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