New roots to formation of nanostructures on glass surface through anodic oxidation of sputtered aluminum

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Received 31 March 2003; revised 19 June 2003; accepted 25 June 2003

Abstract

New processes for the preparation of nanostructure on glass surfaces have been developed through anodic oxidation of sputtered aluminum. Aluminum thin film sputtered on a tin doped indium oxide (ITO) thin film on a glass surface was converted into alumina by anodic oxidation. The anodic alumina gave nanometer size pore array standing vertically on the glass surface. Kinds of acids used in the anodic oxidation changed the pore size drastically. The employment of phosphoric acid solution gave several tens nanometer size pores. Oxalic acid cases produced a few tens nanometer size pores and sulfuric acid solution provided a few nanometer size pores. The number of pores in a unit area could be changed with varying the applied voltage in the anodization and the pore sizes could be increased by phosphoric acid etching. The specimen consisting of a glass substrate with the alumina nanostructures on the surface could transmit UV and visible light. An etched specimen was dipped in a TiO$_2$ sol solution, resulting in the impregnation of TiO$_2$ sol into the pores of alumina layer. The TiO$_2$ sol was heated at $\sim$ 400 °C for 2 h, converting into anatase phase TiO$_2$. The specimens possessing TiO$_2$ film on the pore wall were transparent to the light in UV–Visible region. The electro deposition technique was applied to the introduction of Ni metal into pores, giving Ni nanorod array on the glass surface. The removal of the barrier layer alumina at the bottom of the pores was necessary to attain smooth electro deposition of Ni. The photo catalytic function of the specimens possessing TiO$_2$ nanotube array was investigated in the decomposition of acetaldehyde gas under the irradiation of UV light, showing that the rate of the decomposition was quite large.

Keywords: Anodic oxidation; Sputtered aluminum; Glass surface; Nanostructure; Photocatalyst; Sol–gel process; Electro deposition

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doi:10.1016/S1468-6996(03)00059-7
1. Introduction

Recently nanostructured materials have attracted great interest for their potentiality leading to the unique functions in the optical properties, electronic properties, magnetic properties and mechanical properties. The gas phase synthesis techniques like CVD, MOCVD, sputtering, pulsed laser deposition assisted with masking mechanisms have been used to form nanostructures on substrates [1]. Photo etching technique is also used for making nanopore arrays on material surfaces [2]. These techniques can produce two- and three-dimensional nanostructures and have been the major techniques for the formation of devices in the future.

The anodic oxidation of aluminum has been used as the method to convert the aluminum surface into alumina for the improvement of the chemical durability. The anodic oxidation technique is known as the self-organization process to generate the porous alumina where the nanopores are arranged as perpendicular to the substrate. In these years, the porous anodic alumina has been studied to fabricate the nanostructured materials [3–7]. The anodic oxidation of the thin aluminum film has been studied recently on the sputtered aluminum film on Ta metal [8] and Si [9] metal substrates, resulting in the oxidation of the aluminum layer followed by the oxidation of the substrate.

The authors have been studying the formation of the nanostructures on glass surfaces and have developed the new process in which the sputtered aluminum film on ITO layers on glass substrates was converted into the nanostructures by anodic oxidation [10]. The authors have also been studying the processes to introduce other compounds into nanopores of the anodic alumina using sol–gel technique and electro deposition. The TiO\textsubscript{2} component could be introduced by sol–gel process [11, 12] giving the high efficiency photocatalytic function [13]. The density of the nanopores of the alumina nanostructures on the glass surface was estimated to be about \(1 \times 10^{13}/\text{m}^2\) (\(\sim 600 \text{ Gbit/inch}^2\)) and the introduction of the magnetic components possessing easy magnetization axis perpendicular to the substrate would be applicable to the ultra high density magnetic recording media. The introduction of Ni metal could be attained by electro deposition process and the magnetization characteristics of the Ni nanorods were investigated [14].

In this paper, the new processes were reviewed to compile the new roots for the formation of nanostructures on glass surfaces and to discuss about the possible applications.

2. Experimental details

2.1. Substrates

Pure aluminum (99.99\%) was deposited on a soda-lime-silica glass substrate coated with ITO and SiO\textsubscript{2} protection thin film by RF sputtering. The size of the substrate was \(20 \times 100 \times 1.1\) mm. The thickness of the ITO film and SiO\textsubscript{2} film were 100–130 and \(\sim 15\) nm, respectively. The sheet resistivity of the ITO film was 10–20 ohm. The aluminum layer was deposited at the rate of \(\sim 1.5\) nm/s in 2.5 cycles (0.8 \(\mu\)m per cycle) under the pressure of \(1.0 \times 10^{-3}\) Torr to reach \(\sim 2\) \(\mu\)m in the thickness.

2.2. Anodic oxidation [10]

The aluminum thin film was anodized by a regulated dc power supply in a 10 vol\% phosphoric acid solution or in a 3\% oxalic acid solution or in a 10\% sulfuric acid solution. The specimens were washed by ultrasonic-cleaning in ethanol for 10 min and were anodized in phosphoric acid at a voltage of 130 V at 280 K, in oxalic acid at 40 V at 293 K and in sulfuric acid at 15 V at 283 K. To avoid repetition, the anodic oxide films prepared in phosphoric, oxalic and sulfuric acid solutions are quoted as phosphoric films, oxalic films and sulfuric films, respectively. The setup for the anodization was shown in Fig. 1 together with a model of anodic alumina. Anodic alumina consists of hexagonal cells possessing pores at the centers. Barrier layer is formed at the bottoms of the pores. The part of the films on the substrate was enlarged on the figure and the scale of the specimen did not show the real dimensions. The etching of the anodized specimens were executed by immersing in a 5 vol\% phosphoric acid at 30 \(^\circ\)C for 2–15 min to enlarge the pore size and to remove the anodic alumina barrier layers at the bottoms of the pores (to expose the ITO layer to the electrolyte) for the smooth electro deposition of Ni metal.

2.3. Sol–gel process [11,12]

The TiO\textsubscript{2} sol (\(\sim 5\) wt\%) was prepared from reagent grade titanium isopropoxide, acetylacetone, ethanol and distilled water at a mole ratio of 1:1:20:3. The reaction was carried out at room temperature in the open air. The mixture was stirred for 2 h and stored in a brown bottle at room temperature. Prior to the experiments, the sol solution was aged for 1 week–1 month. Though the color of the sol changed gradually from light yellow to dark yellow, nothing precipitated and the solution was very stable.

In the introduction of TiO\textsubscript{2} sol into the nanopores of the anodic alumina, the specimens were first immersed in ethanol for 10 min and then dipped in the TiO\textsubscript{2} sol at room temperature for 20 min. After 20 min dipping, the specimens were lifted up slowly from the solution. The TiO\textsubscript{2} sol on the back side of the specimen was washed away with ethanol. The specimens dipped in the TiO\textsubscript{2} sol were dried in the air at room temperature for more than 2 h. To obtain porous alumina/titania structure, the specimens were heated in furnace at 100 \(^\circ\)C for 1 h and at 400 \(^\circ\)C for 2 h where the heating rate was 2 \(^\circ\)C/min.
2.4. Electro deposition process [14]

The schematic illustration of the procedures for the electro deposition of Ni is shown in Fig. 2. The electrolyte solution for the Ni electro deposition consisted of 0.38 M NiSO$_4$, 0.13 M NiCl$_2$, 0.65 M H$_3$BO$_4$ and 60 ppm CH$_3$(CH$_2$)$_{11}$OSO$_3$Na, and was adjusted to pH 5.2 with a 20% NaOH solution. The specimens were immersed in distilled water for 1 min to push out the air in the pores with applying ultrasonic wave prior to the electro deposition. The Ni electro deposition was performed at 1.0–1.5 V and 30$^\circ$C for 2–10 min, with stirring. The counter electrode was a pure nickel plate. To get Ni nanorods, the alumina skeletons of the specimens were removed with the etching by 5% NaOH solution.

2.5. Characterizations

The morphology of the samples were observed with a field emission scanning electron microscope (FE-SEM, S-500, Hitachi) with an energy-dispersion X-ray analyzer (EDXA). The thin coating of osmium was applied on the sample surfaces for the discharge during observations. The UV–visible transmission spectra were recorded by a spectrophotometer (U-3500, Hitachi). The crystalline phases were identified with an X-ray diffractometer (XRD, RINT-2000/PC, Cu K$\alpha$, 40 V/40 mA). The transmission electron microscope (TEM, JEM-1010, 100 kV) was used to observe the structures of Ni nanorods. Magnetization curves were measured by a vibrating sample magnetometer (USM, Lake Shore model 7300). The evaluation of the photocatalysis of the TiO$_2$ nanotube array was performed by monitoring the volume of CO$_2$ gas released in the decomposition of acetaldehyde. The experimental system for the evaluation of photocatalytic function was a closed circulating system, in which the specimens were irradiated by UV light and the volume of CO$_2$ gas was determined using a gas chromatography equipped with a mass analyzer. The details of the apparatus were given in Ref. [12]. One of the popular and high performance photocatalysts, Degussa P25, was used as the reference sample. The UV light source was a 200 W Hg–Xe lamp possessing the peak emission at 365 nm.

3. Results and discussion

3.1. Nanostructures on the glass surface [10]

The FE-SEM photographs of the anodic alumina prepared under various conditions are shown in Fig. 3. The details of the preparation procedures of the specimens
were given in the Ref. [14]. The sizes of the phosphoric film etched by phosphoric acid for 30 min were 120–180 nm in diameter. The average pore size of the samples just after the anodization under the same conditions was around 80 nm. The pore diameters of the oxalic film were 40–50 nm. The pore sizes of the sulfuric film were 5–8 nm.

Fig. 4 shows the relationships between the number of the pores in a unit area, the average pore size, the average cell size and the anodizing voltage in the phosphoric film case. The solid curve marked with 'Top' corresponds to the average cell size in the top of the anodic alumina layer while the broken curve marked with 'Bottom' indicates that in the bottom of the alumina layer. The number of the pores increased with decrease of voltage and reached up to about $1 \times 10^{15}/m^2$. The average pore size did not depend on the voltage but the cell size increased drastically with increase of voltage. Tuning of the anodizing voltage can control the size of the cell and the number of the pores. The pore diameter can be enlarged by acid etching.

The pores were formed by self-organization process as perpendicular to the glass substrate. The photographs of the specimens are shown in Fig. 5. The specimen became
transparent after the anodization. The etching treatment made the specimen a little frosty. That is considered to be derived from the slight corrosion of the ITO film by the etching. The transmission spectra of the phosphoric film specimens are shown in Fig. 6 [10]. The dashed line means boundary between visible region and UV region. The anodic alumina film on the glass gave 90% transmission in the visible region. The waving of the spectrum is originated from the interference taking place within the specimen.

3.2. Introduction of TiO$_2$ sol into nanopores [11]

Fig. 7 shows the schematic illustrations, the photos of the specimens and the SEM photos in the process for the synthesis of the TiO$_2$ nanotube array on the glass. After acid etching, the sol was introduced into pores. The change of the thickness of the wall of the SEM photographs indicate that the inside wall of the pores were coated with the TiO$_2$ sol. The photo shows that the transparency was kept after the impregnation. The transmission spectrum was given as the lower curve in Fig. 6 marked with ‘Al$_2$O$_3$/TiO$_2$ Nanostructure’, showing the transmission of 30–80% in the visible region. The surface area of the specimen was estimated to increase by ~50 times from the calculation based on the simple geometry. The TiO$_2$ formed in the process was identified to be anatase by the X-ray diffraction. Introduction of TiO$_2$ was also tried on oxalic films and sulfuric films. TiO$_2$ sol impregnated into the oxalic film was able to be converted into anatase by heating, while it was not introduced into the sulfuric film because of the too small pore size.

3.3. Evaluation of photocatalytic function [13]

The relative value of the volume of the released CO$_2$ gas was plotted against the irradiation time of UV light in Fig. 8. All the data were normalized to the specimen area of 1 cm$^2$. 100% level corresponds to the CO$_2$ quantity which was yielded by the decomposition of the all the acetaldehyde introduced into the closed test system. The impregnated anodic film on the glass (the top curve in Fig. 8) gave the very quick decomposition rate larger by ~13 times than that of Degussa P25 (the bottom curve in Fig. 8), which is one of the high efficiency photo catalysts commercially available. The quick decomposition rate is believed to be derived from the increase of the quantity of TiO$_2$ in a unit area and also from the increase of the light irradiation efficiency based on the transparency of the substrate. The plateau of the decomposition after 60 min is considered to be resulted from the slow down of the decomposition reaction due to the drastic decrease of the acetaldehyde gas. The TiO$_2$
impregnated oxalic film also showed the photo catalytic function better than the Degussa P25 (the intermediate curve in Fig. 8). The surface area of the oxalic film is believed to be larger than that of phosphoric film, but the decomposition rate was the intermediate values among the three films. This result suggests that the increase of the irradiation efficiency is effective to enhance the photo catalytic function more than the increase of the surface area or the increase of TiO₂ in a unit area.

3.4. Introduction of Ni into nanopores [14]

The cross sectional SEM photographs of the phosphoric film and oxalic film are shown in Fig. 9 (deposition time: 2 min). The Ni deposition was performed directly on the ITO film. When the anodic alumina barrier layer remained, the electro deposition could not be performed stably due to insulation of the amorphous alumina. The removal of the barrier layer by etching or the exposure of the ITO layer to the electro deposition solution is necessary to get stable electro deposition in the pores. The SEM photos of the Ni nanorod arrays, which were obtained after dissolution of anodic alumina skeletons, were summarized in Fig. 10. The phosphoric film, the oxalic film and the sulfuric film gave the nanorods of ~150, ~50, and ~18 nm in diameter, respectively. The average aspect ratios are ~14 for the phosphoric film, ~36 for the oxalic film and ~67 for the sulfuric film. The anodic alumina could work as the nanostructure templates to form metal nanorod arrays on glass surfaces.

3.5. Applications

The TiO₂ impregnated anodic alumina on glass surfaces can be applied to the high efficiency photo catalysts to decompose organic compounds. The test has not been tried yet, but the anodic film TiO₂ catalyst is believed to work on the decomposition of dioxin compounds. Although some optimizations of the procedures will be necessary, the anodic oxidation can be applied to large substrates like window glasses and the curved substrates like fibers. The high efficiency photo catalytic window glasses or fibers could be fabricated.

The TiO₂ impregnated anodic films on glass substrates can be applied to the preparation of dye sensitized solar cell arrays. The nanostructure and the transparency of the substrate are favorable to enhance the interaction of TiO₂ film and light. The ITO layer works as a cathode of the cell and the top of the anodic film is covered with a conductive substrate for an anode.

The pores stuffed with the magnetic materials, which give the magnetization perpendicular to the substrate stronger than the in-plane magnetization, would work as magnetic recording spots. Taking that the density of the pores of the anodic films was about 600 Gbit/inch² into account, the anodic films embedded with appropriate magnetic substances could be applied to the ultra high density magnetic recording media.

Moreover the hexagonal cells possessing magnetic material in the pores of the anodic alumina film can be decomposed into isolated cells which would be used as nanosize magnetic heads for the new ultra high density magnetic recording system.
4. Conclusion

The anodic oxidation of the sputtered alumina on the glass substrate was fruitful process to build up the nanostructures on glass surfaces. The introduction of the compounds into nanopores could be attained with the sol–gel dipping process and the electro deposition technique. The embedding of the components into the nanopores could endow the glasses with the photo catalytic functions and would be applicable to the ultra high density magnetic recording and dye sensitized solar cells. The photo catalyst prepared in this study showed the decomposition rate of acetaldehyde larger by one order of magnitude than that of the Degussa P25. The anodic oxidation process, the sol–gel coating process and the electro deposition process are principally applicable to general curved substrates and large substrates. The new process does not require the special and expensive apparatuses like high power lasers, nanometer range precise manipulators etc. Therefore the process is believed to have an advantage over the other nanomachining processes in the applications and the commercial productions.

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