Fabrication of antireflection-structured surface using vertical nanowires as an initial structure

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An antireflection structure was fabricated using vertically synthesized iron oxide nanowires as an initial structure. Iron oxide nanowires can be synthesized by simply annealing a thin Fe film in air. The authors propose a process for transforming these nanowires into an array of cone: An additional thin Cr film is deposited onto the nanowires and then etched by reactive ion etching. As a result of the redeposition of Cr, the vertical nanowires were successfully transformed into conical structures. This antireflection nanostructure is replicated onto a polymer surface by thermal nanoimprinting, and the replicated surface exhibited low reflectivity at all visible wavelengths. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3467506]

Since antireflection (AR) nanostructures[1,2] were first demonstrated as a broadband coating of optical elements, they have been researched and expected to be used for coating optical devices such as flat-panel displays, lenses, optical fibers, light-emitting diodes, and solar cells. AR structures have the advantages of a low dependence of their performance on wavelength and incident angle compared with multilayer-dielectric-film coatings. AR nanostructures have a refractive-index gradient perpendicular to the surface, i.e., a nanocone or nanohole array. The pitch of the structure must be narrower than the wavelength of light and the height should generally be higher than twice the pitch. Meanwhile, nanoimprinting[3,4] has recently been developed as a low-cost method of fabricating nanostructured surfaces, in which a nanostructured mold is pressed on a polymer and to replicate the nanostructures on the polymer surface. As a result of the development of nanoimprinting techniques, AR surfaces can also be fabricated by nanoimprinting. In the many basic studies on the nanoimprinting of AR surfaces, molds with a nanohole array of approximately 250 nm pitch have been fabricated by electron beam (EB) writing and subsequent dry etching, although the mold has also been fabricated by other approaches such as by coating a monolayer colloidal particle mask[5] or depositing a self-organized random mask.[6,7] Because these techniques do not use expensive lithography, the sample size is not limited by the wafer lithography system. Moreover, random nanostructures also have the advantage of exhibiting no diffraction effect.

One-dimensional nanostructures[8,9] made of crystalline metal oxides such as ZnO, indium tin oxide, Fe_2O_3, V_2O_3, NiO, CuO, and $W_{18}O_{49}$ have recently been investigated as promising materials for new nanodevices. Nanowires of these oxides can be synthesized by the simple annealing of metal substrates or by chemical vapor deposition and have a width of 10–100 nm and a length of 0.1–10 μm. These nanowires have unique electronic and chemical properties and are expected to be used in various nanoelectronic devices such as field emitters,[10] gas sensors,[11] magnetic recording,[12] and electrochromic devices.[13] On the other hand, there has been little research on the use of these nanowires as structures for controlling electromagnetic waves. In this letter, we propose a novel method for the low-cost fabrication of a nanoimprinting mold with random AR nanostructures from vertical nanowires on a surface.

We have demonstrated that α-Fe_2O_3 (hematite) nanowires can be synthesized by the atmospheric heating of a sputtered or thermally evaporated thin Fe film.[14] An advantageous part of this method is that no catalysts are required in the synthe-

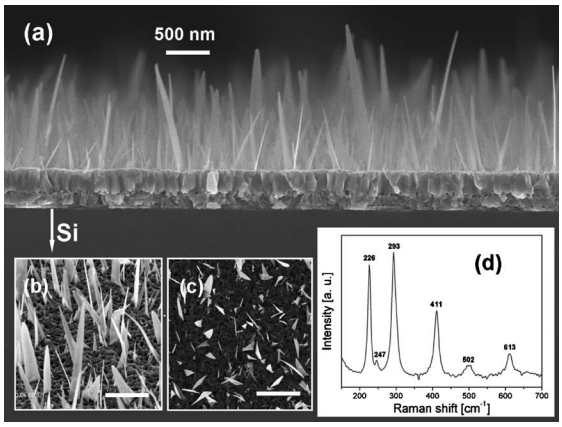

FIG. 1. Iron oxide nanowires synthesized from sputtered thin Fe film. SEM image of cross section (a), 45°-tilted view (b), top view (c), and Raman spectrum of the nanowire substrate (d).

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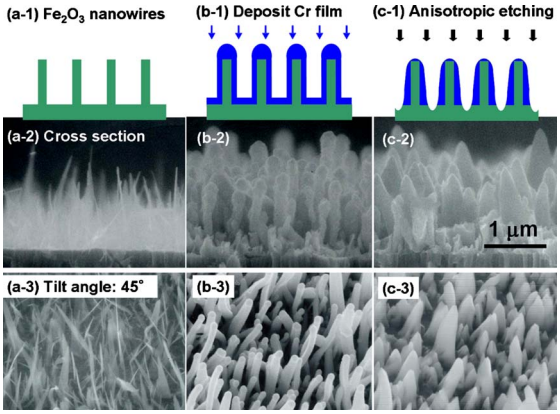

FIG. 2. (Color online) Schematic of fabrication of array of conical structures; nanowire synthesis (a)(1), Cr deposition (a)(2), and anisotropic CHF_3 etching (a)(3). Cross-sectional SEM images [(b)(1)–(b)(3)] and 45°-tilted views [(c)(1)–(c)(3)] at each step.

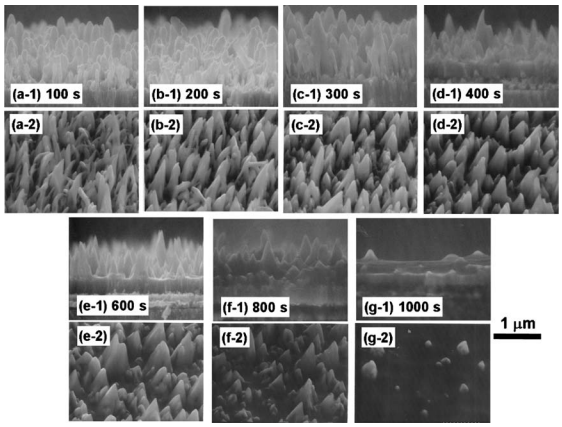

FIG. 3. SEM images of array of conical structures after various etching times (100/200/300/400/600/800/1000 s).

sis. Figure 1 shows iron oxide nanowires synthesized from a thin Fe film with a thickness of 200 nm deposited on a Si substrate. A Cr film (10 nm thickness) was also deposited between the Si substrate and the Fe film to prevent the detachment of the Fe film. The Fe/Cr film was formed by rf magnetron sputtering with Ar gas. The base pressure of the chamber and the sputtering pressure were 1×10^{-2} and 5×10^{-1} Pa, respectively. After sputtering, the substrate was loaded into a furnace and annealed in an atmospheric-pressure flow of air. The furnace was heated to 375 °C in 1 min then was maintained at this temperature for 30 min. Atmospheric-pressure air with humidity of 40%–60% flowed through the inlet at a rate of 2.5 l/min to maintain a pressure of 0.1 MPa. Figures 1(a)–1(c) show scanning electron microscopy (SEM) images of a cross section of the substrate and nanowires, a tilted view (45°), and a top view, respectively. The thickness of the Fe film increased to 400 nm owing to its oxidation by heating in air. Figure 1(d) shows its Raman spectrum. The peaks are due to α-Fe_2O_3.[15,16]

These nanowires have tapered structures with a suitable pitch and height for use as AR nanostructures; however, they are too thin and the bottom face between the bases of the nanowires which is parallel to the substrate make the nanostructures unsuitable for use as an AR surface. We propose a novel process for transforming the vertical thin nanowires into an array of cones without a bottom face involving an additional deposition followed by anisotropic dry etching. Figure 2 shows a schematic of the fabrication method and images of the nanowires after each step of the process: [(a)(1)–(a)(3)] after synthesizing nanowires, [(b)(1)–(b)(3)] after depositing a Cr film, and [(c)(1)–(c)(3)] after etching with CHF_3. The Cr film was formed by rf magnetron sputtering under the same conditions as those for the Cr/Fe film. The thickness of the Cr deposited on the flat face was 50 nm. CHF_3 etching was carried out using inductively conductive plasma (reactive ion etching (RIE) apparatus (CE-300I, ULVAC, Ltd.). The etching power and bias power were 400 and 150 W, respectively. The CHF_3 pressure was 0.5 Pa and the etching time was 300 s. As shown in Fig. 2(b)(2) and Fig. 2(b)(3), Cr was deposited to a greater thickness on the upper parts of the sidewalls than on the lower parts, with most Cr being deposited at the tops of the nanowires. This is due to the concentration of the electric field at the tops of the nanowires and the isotropic diffraction of Cr atoms upon the collision of Ar molecules. As shown in Fig. 2(c)(2) and Fig. 2(c)(3), the pillars became conical upon etching. The Cr atoms etched from the bottoms and sidewalls of the nanowires can be redeposited on the sidewalls. This redeposition effect is larger toward the bottom of the nanowires. As a result, the array of cones has negligible face parallel to the substrate between the cones.

We show the arrays of cones obtained after various etching times (100/200/300/400/600/800/1000 s) in Fig. 3. After 100 s, the apex of the nanowires had become sharper than that of the original structures. After 200 s, the smaller nanowires had combined with neighboring nanowires. The Cr atoms etched from the bases and lower slopes of the nanowires were redeposited on the bases. The nanowires consequently became wider at the bases and were transformed into tapered conical structures, as shown in the image obtained after 300 s etching. After 400 s, the shorter nanowires had disappeared and the remaining nanowires had become shorter. After 400 s, it was possible for the Cr layer to be etched from the shorter nanowires. Because the etching rate of Fe_2O_3 was lower than that of Cr, the shorter nanowires disappeared more quickly. Among the samples obtained in this way, the sample obtained after 300 s etching has 200–400 nm pitch and 500–1500 nm height; it would be optimum structure for antireflection. Note that by depositing other materials, changing the thickness of the depositing material or using other deposition methods such as evaporation or ion plating, other final structures may be designed.

To confirm the AR property of the nanostructures, we thermally replicated the structures onto the surface of a polymethyl-methacrylate (PMMA) film (Acryplene, Mitsubishi Rayon Co., Ltd., thickness: 100 μm). The sample obtained after 300 s was used as a mold and coated with a lubricant (Optool HD-1100, Daikin Chemical, Ltd.) before the replication. We used a thermal nanoimprinting system

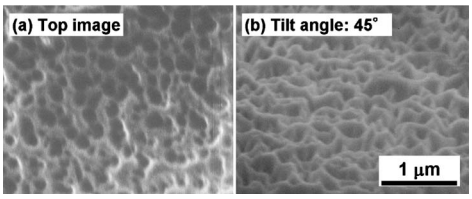

FIG. 4. SEM images of imprinted PMMA film; cross section (a) and tilted view (b).

(VX-1000N-NN, SCIVAX Co, Ltd.). The pressure, imprint temperature, and pressing time were 5 MPa, 160 °C, and 60 s, respectively. Figure 4 shows SEM images of the imprinted PMMA surface. Nanoholes corresponding to the nanocones of the mold were observed. Because the nanoholes have a high aspect ratio and are located randomly, it is difficult to quantitatively measure the imprinted structures using atomic force microscopy or cross-sectional SEM observation. We measured the reflectivity of the imprinted surface using a spectrophotometer (CM-2600d, Konica Minolta Sensing, Inc.). Figure 5(a) shows the reflectivities of the flat PMMA surface and the imprinted surface. The reflectivity of the flat surface was drastically lower than that of the imprinted surface over the entire range of visible wavelengths. When measuring the reflectivity, the reverse side of the PMMA film was attached on a black PMMA plate using a double-sided tape with the same refractive index as PMMA (1.5). Figure 5(b) shows optical photographs of PMMA films with a flat surface and with an imprinted surface reflecting fluorescent light. The intensity of the fluorescent light reflected from the PMMA surface was clearly reduced by imprinting the nanocones.

Furthermore, we replicated the PMMA replica mold onto an ultraviolet (UV)-curable polymer (UV-curable polyurethane acrylate resins for nanoimprinting, Hitachi Chemical, Ltd.). The replica mold was fabricated by depositing a thin Cr film (thickness: 50 nm) on a PMMA replica that was

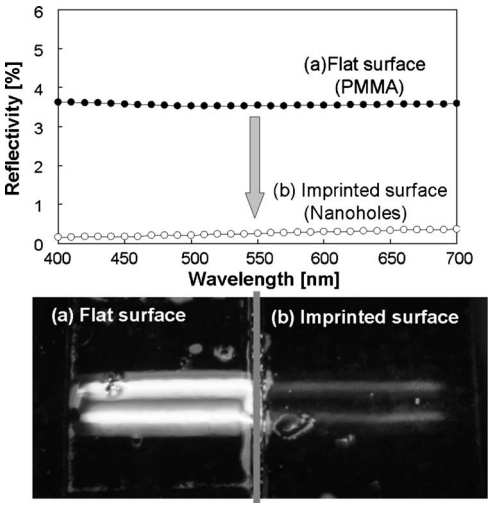

FIG. 5. Reflectivities and optical images of PMMA flat surface (a) and imprinted surface (b). The films were attached on a black PMMA plate using an optically matched tape and an image of fluorescent light reflected from each film was obtained.

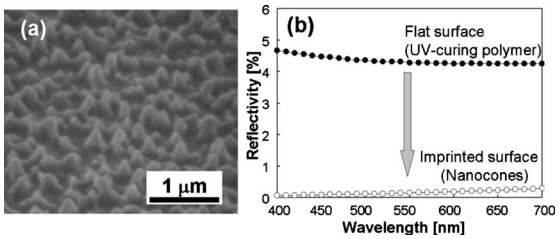

FIG. 6. UV-curable polymer imprinted using the PMMA replica mold (Fig. 5). SEM image taken from 45° (a) and reflectivities of flat and imprinted surfaces (b).

imprinted by the above-mentioned method. First, the UV-curable polymer was dropped onto a polyethylene terephthalate (PET) (thickness: 100 μm) film. Second, the replica mold was pressed onto the PET film. Finally, UV light was irradiated from the reverse side of the PET film. A similar dramatic decrease in reflectivity was obtained for the imprinted PET film as shown in Fig. 6.

In summary, we proposed a method for transforming iron oxide nanowires into an AR surface consisting of subwavelength-pitched cones. In this method, the width of iron oxide nanowires vertically synthesized from a flat surface was increased by the additional deposition of Cr, then the nanowires were etched by RIE with CHF_3. As a result of the redeposition of Cr and anisotropic etching, the straight nanowires were transformed into conical structures with wide bases and sharply pointed apexes suitable for use as an AR surface. The nanostructures with various sizes can be designed by selecting different nanowires as the initial structures and different deposition and etching conditions. This method will lead to low-cost fabrication of large-area imprinting mold with random AR surface because this method does not need lithography. Furthermore, using this method, the nanostructures can also be fabricated on nonflat surfaces and the mold for imprinting of the three-dimensional shapes such as lenses, microlens arrays, or gratings, on which EB, photolithography cannot easily be applied.

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