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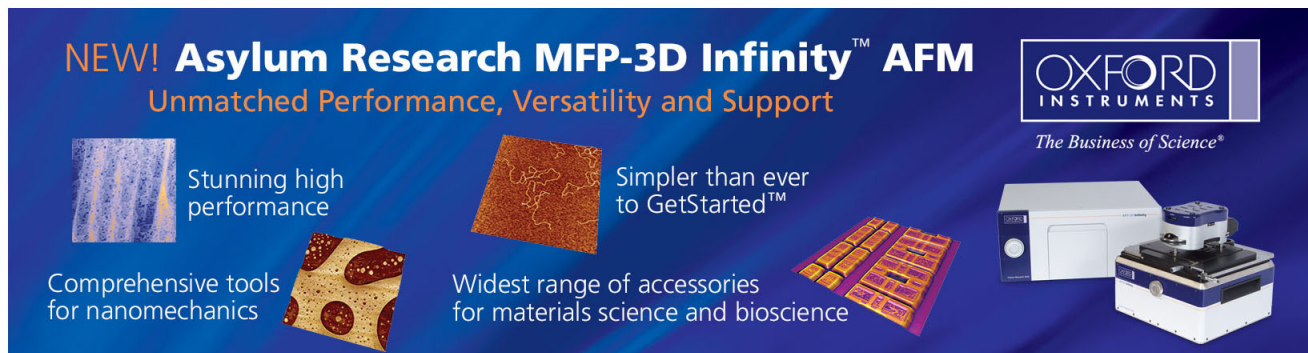
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Self-organized tantalum oxide nanopyramidal arrays for antireflective structure

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A self-organized tantalum oxide nanopyramidal structure without tedious semiconductor processing is proposed in this letter. Construction of pyramid arrays with a close-packed periodicity of 200 nm and a height of 200 nm was achieved by the anodic alumina template method directly on the substrate. The tantalum oxide nanopyramidal structure was formed as the underlying tantalum film oxidized and localized precisely by the pore of alumina. The reflectance from the spectroscopic measurement suggests that the nanopyramidal array structures have more broadband antireflection (<2%) than the nanodot arrays and thin film structures. © 2007 American Institute of Physics.

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The fabrication of self-organized nanodot arrays onto a surface has attracted growing interest due to their low-cost realization in functional structures and in the fields of nanodevices such as optoelectronics,¹ information storage,² and sensing.³ A variety of alternative methods has been proposed for the self-organized formation of nanodot arrays onto a surface such as diblock copolymer,⁴ Stranski-Krastanow growth,⁵ and colloidal self-assembly.⁶ The discovery of self-ordered porous alumina in 1995 by Masuda and Fukuda⁷ consisted of vertical pore channel arrays with a high density hexagonal packing structure which were obtained by anodic oxidation of aluminum in an acidic electrolyte. In a previous work, nanodot arrays on surfaces have been fabricated using an extremely thin anodic aluminum oxide template that served as a mask for evaporation of nanodots onto the surface.⁸ A more versatile and robust approach is to oxidize the underlying metal⁹ or silicon¹⁰ to form oxide nanodot arrays directly on the surface. The oxide nanomaterial possesses the advantages of corrosive and thermal oxidation tolerance.

Low-cost and high-performance antireflection coatings are required for solar cells and display devices. Conventionally, the optical thin film structures are proposed to achieve the purpose of antireflection (AR). Both of the following conditions are needed:^{11,12} (a) the thickness of the coating is $\lambda/4$, where λ is the wavelength of incident light, and (b) an ideal homogeneous single-layer AR coating satisfies the following condition: $n_C = (n_A n_S)^{1/2}$, where n_C , n_A , and n_S are refractive indices of the coating film, air, and substrate, respectively. The challenge of the thin film structure is the narrowband AR at the wavelength of interest. It is inevitable that narrowband AR will extend to broadband AR from the improvement of surface structure to nanoscale. Instead of a homogeneous thin layer, the texturing techniques achieved by tedious semiconductor manufacturing have been proposed.^{13,14}

The thickness and optical constants of multilayered optical coatings should be precisely controlled for broadband antireflection coatings.¹² Traditionally, the wet etching method is used to fabricate the antireflective V-groove profile structures on a single-crystal silicon surface by etching with an alkaline solution.¹⁵ However, the parameters of temperature, sodium hydroxide concentration, and 2-propanol concentration should be well controlled to ensure the suitability of etching rate for broadband AR structure. More modern approaches are based on semiconductor processing including reactive ion etching,¹⁶ an expensive lithography technique,¹⁷ and the surface porous silicon structure.¹⁸ However, in reference to the aforementioned techniques, the more complicated the technique used to improve the desired properties, the higher the production cost and time requirement. Hence, the low cost, effective approaches for depressing the reflection and the high efficiency of nanometer structures would be desirable. More investigation is needed in these areas.

Previous research indicated that the suitable broadband AR structure was a pyramid of silicon.^{16,19} The pyramid structure exhibits a graded index property relative to the thin film structure with the abrupt index. In this study, we demonstrate a simple method to fabricate the very stable pyramidal structures with a low cost and large area by self-organized tantalum oxide nanodot arrays through an anodic alumina template. The hexagonal close-packed arrangement of subwavelength pyramidal structures with low reflection in the 300–900 nm wavelength regimes can be easily achieved.

The fabrication process of pyramidal nanodot arrays is depicted in Fig. 1. The tantalum and aluminum films were sequentially deposited onto a cleaned 6 in. silicon wafer by a sputtering system. Anodization was carried out in 2M phosphoric acid solution under a voltage of 100 V. During the anodizing process, the electrolyte was rigorously stirred or recycled using a pump system. The anodizing reaction must be immediately stopped when a distinct color change in the sample surface occurs, which took only 35 s. The alumina film is then removed in 5 wt % phosphoric acid solution under room temperature.

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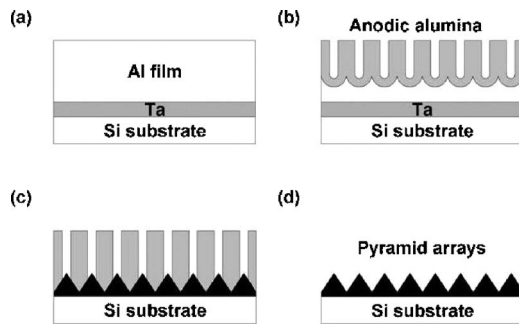


FIG. 1. Schematic diagram of the fabrication process of the tantalum oxide nanopyramidal arrays on a Si wafer.

Figures 2(a) and 2(b) show the slide-view scanning electron microscopy (SEM) (JEOL JSM-6700F) images of pyramidal nanodot arrays at various anodization periods. The insufficient 30 s anodization time in Fig. 2(a) cannot form the close-packed pyramidal arrays and exhibits poor AR. The tantalum oxide bulges jugged out over the residual aluminum. This observation is attributed to the Al residue from the incomplete anodization. In contrast, the pyramidal structure after a 35 s anodization time with a $2 \times 10^9/\text{cm}^2$ density in Fig. 2(b) is very dense with an average diameter of 200 nm and an average height of 200 nm. The close-packed pyramid structure of 200 nm period, which is the surface-relief grating with a period smaller than the incident light wavelength, behaves as an advantaged AR surface. Horizontal projections of the bases look like distorted hexagons or pentagons rather than the circles under pores in Fig. 2(c). In contrast, the shape of the nanostructure presented here is a pyramid instead of a hemisphere reported in other records.^{9,20} Figure 2(d) shows the cross-sectional transmission electron microscopy (TEM) (JEOL JEM-2100F) image of the bottom of the alumina pores. An isolated pyramid structure embedded at the interface between porous alumina and the underlying layer is seen. The inset in Fig. 2(d) with the selected area electron diffraction (SAED) image shows an amorphous

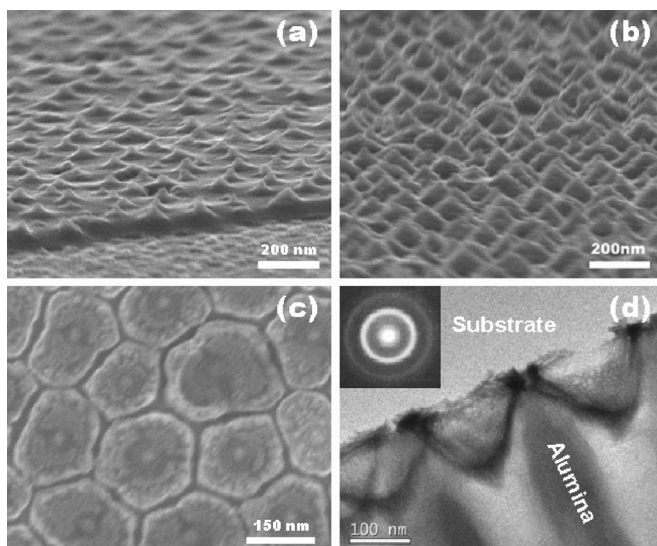


FIG. 2. (a) Slide-view SEM image of the tantalum oxide nanopyramidal arrays with 30 s anodization time. (b) Slide-view SEM image of the tantalum oxide nanopyramidal arrays with 35 s anodization time. (c) Top-view SEM image of the tantalum oxide nanopyramidal arrays. (d) TEM image of the tantalum oxide nanopyramidal arrays under the porous alumina film, the inset is the SAED image.

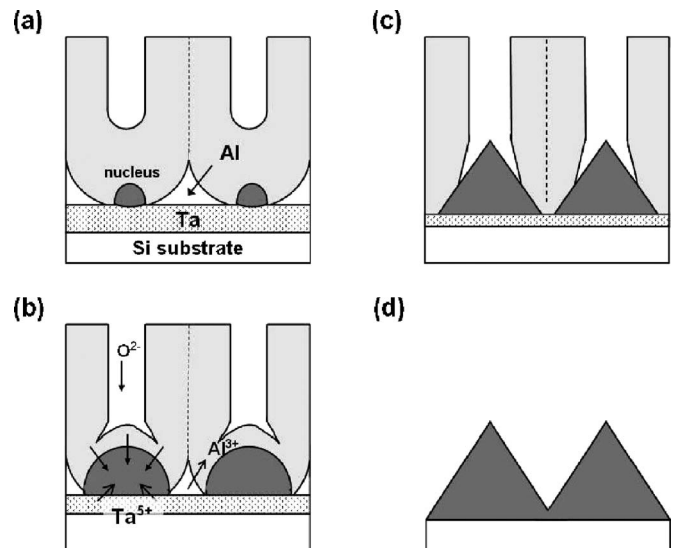


FIG. 3. Schematic diagram to describe the formation mechanism of the tantalum oxide nanopyramidal arrays at the Ta/Al interface.

structure of tantalum oxide pyramidal arrays, and the result conforms to the literature.²¹ The chemical composition of the self-organized pyramids is expected to be the composition of nonstoichiometric TaO_x with Ta_2O_5 at the surface and coexistence of different oxidation states of tantalum inside.²⁰

The anodization mechanism for the formation of nanopyramidal tantalum oxide structures was presented as follows. The top aluminum layer in Fig. 3(a) is oxidized to alumina, accompanied by the outward migration of Al^{3+} and inward diffusion of O^{2-} driven by the applied electric field, leading to the vertical pore channel growth. As the oxide barrier layer at the bottom of the pore approaches the Ta/Al interface, the O^{2-} migrating inwards through the alumina barrier layer is injected into the Ta layer and the tantalum oxide nanodot is formed as the released Al^{3+} migrating outward through the remaining barrier layer are expelled, for the most part, into the electrolyte [see Fig. 3(b)]. The growth of the tantalum oxide nanodot resulting from the continuously injecting O^{2-} accompanies the volume expansion of anodic oxidation while the barrier layer is simultaneously thinned by the wet etching of the phosphoric acid. The continuous consumption of the adjacent aluminum enhances the expansion of nanodots and, simultaneously, is accompanied by dissolution of the barrier layer until the electrolyte contacted the top of nanodots directly without a barrier alumina layer [see Fig. 3(c)]. The direct contact of tantalum with the electrolyte causes further oxidation of tantalum. Although the top of the nanodots can reach the electrolyte, the residual alumina of sideward pores blocks the growth of the base part of the nanodots. As a result, a pyramidlike nanodot array appeared, as shown in Fig. 3(d). We are unaware of any other report describing the fabrication of nanopyramidal tantalum oxide arrays for an AR purpose, especially with a self-organization approach.

We prepared various samples with bare silicon, 200 nm tantalum oxide thin film,²¹ a nanodot array,²⁰ and a nanopyramidal array for AR evaluation. Figure 4 shows the reflection spectrum as a function of the wavelength with different surface texturing structures. The surface of silicon and tantalum oxide without a nanostructure exhibits a strong reflection. Interestingly, the surface with the nanopyramidal or nanodot

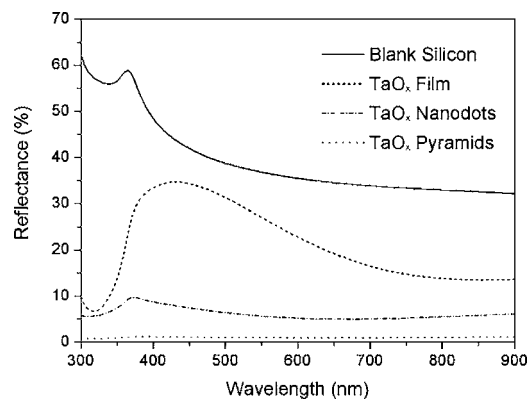


FIG. 4. Spectroscopic measurements of broadband reflectance for the blank silicon wafer, the anodic tantalum oxide film, the tantalum oxide nanodot array, and tantalum oxide nanopyramidal arrays, respectively.

morphology demonstrates better AR performance than the film structure. This observation suggests that the pyramidal array of tantalum oxide in nanometer dimension possesses a more graded index property than the thin film structure with the abrupt index. By means of the pyramid structure, the reflectance of the film is uniformly reduced to below 2% in the wavelengths between 300 and 900 nm. In addition to a better AR viewpoint, the tantalum oxide materials also exhibit better corrosive tolerance and thermal oxidation tolerance than the well-known silicon-based materials.

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