Spontaneous Ordering of Oxide Nanostructures

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ABSTRACT

We report the spontaneous formation of uniformly distributed arrays of "tips" (tall conical hillocks) upon oxidation of palladium (Pd) thin films. The formation of the palladium oxide tips depended on the thickness and granularity of the Pd film and on annealing and oxidation conditions. The height of the tips increased from 0.5 to 1.2 micrometer and their height distribution became broader as the Pd film thickness increased from 40 to 200 nanometers while their density decreased from $55x10^6$ to $12x10^6$ per square centimeter. Enhanced photoelectron emission from locations corresponding to the "tips" suggests their possible use in field emission applications.

In contrast to artificially ordered schemes, such as those currently used in integrated circuits, "self-assembled" processes hold the promise to enable the creation of complex, next-generation of device architectures that rely on the intrinsic ability of the system to organize itself into ordered patterns. Many inorganic systems display microstructural evolution that resembles "self-assembled" processes, for example, dendrite formation in melts, spinodal decomposition in alloys, martensitic twins in metallic and ceramic alloys, where the "assembly " process is driven by thermodynamic and kinetic considerations.

We report the "self-assembly" of micrometer-scale hillocks of conducting palladium oxide (PdO_2). Formation of hillocks in metal films is generally understood to be due to relaxation of thermal expansion mismatch stresses between the substrate and the film (*1*). The compressive stresses that develop during heating lead to diffusion of metal atoms either through the lattice (*2,3*), or along grain boundaries (*4*) leading to the formation of hillocks. Typically discrete, isolated hillocks of the metal form. We report results of experiments aimed at exploiting hillock formation to create arrays of high aspect ratio hillocks (or tips) of materials that may enable future, self-assembled nano-technologies. We have found that this is indeed possible via the oxidation of simple metal thin films such as Pd, Ir, In, and Fe that can form oxides with anisotropic crystal structures. The anisotropy of the oxide promotes oxygen diffusion along certain crystallographic planes as opposed to others. The large volume change accompanying oxidation of these metals leads to large compressive stresses that are relaxed by the formation of hillocks which are up to ~ 2μm high in some cases. We use Pd as an illustrative example of the formation dynamics of such hillocks. Pd metal films (40 to 200 nm thick) were deposited by pulsed

laser ablation at room temperature in 10^{-6} torr vacuum on oxide substrates such as MgO and $LaAlO_3$ and subsequently annealed in oxygen at temperatures between 600 and 900°C. The films were characterized using x-ray diffraction (XRD), atomic force microscopy (AFM), and photoelectron emission microscopy (PEEM).

Fig. 1 shows an AFM image of a polycrystalline Pd film (120nm) deposited on a $LaAlO_3$ substrate after it has been annealed in O_2 at 900°C for 1 hour. It reveals that oxidation is accompanied by the formation of a uniform array of surface features (tips) that resemble the Si (*5*,*6*) and Mo (*7*) cones in a field emitter array and, on different scale, InAs islands on GaAs (*8*). Notice that the tips are approximately 1μm tall and uniformly spaced with a periodicity of ~ 2μm. XRD studies of these films indicate that the entire Pd film is oxidized and that the tips are polycrystalline palladium oxide structures, so we assume that the tips are isolated and the surface seen in the AFM image is that of $LaAlO_3$. They are distinctly different from the hillocks reported earlier in their periodicity, height and composition. The hillocks reported in metal thin films are generally discrete and isolated (for example a single tip over several millimeters) and their height is always less than ~ 100nm (*1*).

To quantify the parameters governing hillock formation, we carried out several simple experiments on Pd thin films. The first set of experiments was aimed at understanding the effect of film granularity on the formation of these tips. Pd films, 800Å thick were grown on single crystal {100} MgO surfaces at (i) room temperature to obtain a polycrystalline microstructure, and (ii) at 725°C to obtain epitaxial [001] growth, which was confirmed

by ϕ angle x-ray scans. They were subsequently annealed either in oxygen or in vacuum at 900^{o}C for 1 hour to create the surface morphologies. Vacuum annealing shows less than 100 nm high hillocks on the surface (Fig. 2A), which were confirmed by XRD to be Pd metal. The film annealed in oxygen (Fig. 2B) is very different from the film imaged in Fig. 1. There is very little indication of the formation of hillocks and it appears that only the roughness of the film has increased. Polycrystalline Pd films showed significantly different behavior. Vacuum annealing forms hillocks ~ 150nm high (Fig. 2C); oxygen annealing shows 1μm tall hillocks (Fig. 2D). Because tips are formed only when the starting Pd film is polycrystalline, transport of Pd atoms or ions may be more rapid by grain boundary diffusion.

The spontaneous ordering of semiconductor nanostructures is an intensely investigated field and it is well established that long-range elastic interaction is the driving force for ordering (*9*). However, the details regarding the ordering of such arrays are highly debated involving thermodynamic and kinetic considerations and therefore are not discussed here. Nevertheless, the above experiments demonstrate one important difference between the tips formed in this study and the hillocks formed in metal and semiconductor films. In metals, the hillocks are reported to form due to relaxation of compressive stresses arising due to thermal expansion mismatch between the substrate and the film (*1*). In our case hillocks formed with similar heights and spacing on both $LaAlO_3$ and MgO substrates, which have a thermal expansion coefficient of $10x10^{-6}$ / ^{o}C (*10*) and $13.8x10^{-6}$ / ^{o}C (*11*) respectively. Pd has a thermal expansion coefficient of ~ $11.76x10^{-6}$ / ^{o}C (*12*), which leads to a compressive stress in the case of $LaAlO_3$ but a

tensile stress in the case of MgO. This difference implies that the source of the driving force for forming hillocks and its magnitude is very different in our case. The oxidation of Pd to PdO_2 is accompanied by a 38% volume change, which introduces compressive stresses that are significantly larger as compared to thermal expansion mismatch and is the primary cause leading to the formation of tips.

To understand the factors that control the size (base diameter) and height distribution we studied the evolution of these parameters with thin film processing conditions including film thickness, annealing temperature, and ambients. Figure 3 illustrates the effect of film thickness on the average height of the tips. What we observe is a progressive increase in the height of the tips, with an average height as large as ~ 1.3μm for the thickest film (Fig. 3A). After oxidation, the height distribution of the tips for the 200nm Pd film and the 40nm Pd film (Fig. 3B) show that although the average height of the tips becomes greater with increasing film thickness, the shape of the distribution curve for the tip height becomes broader. This result suggests that thinner films would lead to a narrow distribution of tips and implies that high aspect ratio tips of PdO_2 can be self-assembled with this process. Also plotted in Fig. 3A is the density (number of tips of average height and above) which decreases from ~ $55x10^6$ to ~ $12x10^6$ tips/cm^2. With increasing film thickness, we observed that the size (base diameter) distribution becomes narrower. These observations are consistent with an Ostwald ripening (*13*) process suggesting that the tips are approaching a specific mean size.

One potential application of these arrays is as field emitter arrays for vacuum microelectronic devices. The possibility that large arrays can be self-assembled using simple thin film processes without the need for expensive lithography makes them interesting for the field emission display industry (*14*). Currently, metal field emitters are fabricated using an elaborate process (the Spindt process (*7*)) involving photolithographic definition of individual emitter wells and the subsequent deposition of the refractory metals to form the periodic arrays of emitters. An intrinsic feature of the Spindt process is the need to carry out expensive micrometer or sub-micrometer photolithography, which is not cost effective for large-area displays. To explore the feasibility of field assisted electron emission, we obtained PEEM images from these arrays under an applied field of 30kV/cm and UV light of energy, ~ 5eV. Because the surface work function of PdO_2 is ~ 3.9eV, (*15*) the tips were expected to emit electrons under these conditions. The PEEM image (Fig. 4A) shows a distribution of bright spots with a typical spacing of about 1.5 to 2.5μm, which is consistent with the spacing of the tips as measured from AFM images (Fig. 4B). The less bright spots are perhaps emission from the edges of the tips. Analysis of bright field patterns in the PEEM images reveals the bright field spot density to be ~ $47x10^6$ tips/cm^2. This result is consistent with the density of tips determined from the AFM images for the same sample, which we estimate (number of tips of average height and above) to be ~ $46x10^6$ tips/cm^2. This density of tips or field emitter cones is well within the specifications for current field emission displays, which requires ~ $6x10^6$ tips/cm^2 based on 1μA current density for each sub-pixel (50μm by 300μm) for a 15inch SVGA monitor (*14*). To further justify the use of these tips as field emission arrays, we have controlled the tip-to-tip distance, their aspect ratio and tip radius by controlling the

thickness and the grain size of the starting Pd film. Finally, these emitters can be gated using a scheme similar to that used for Si field emitter arrays (*5*).

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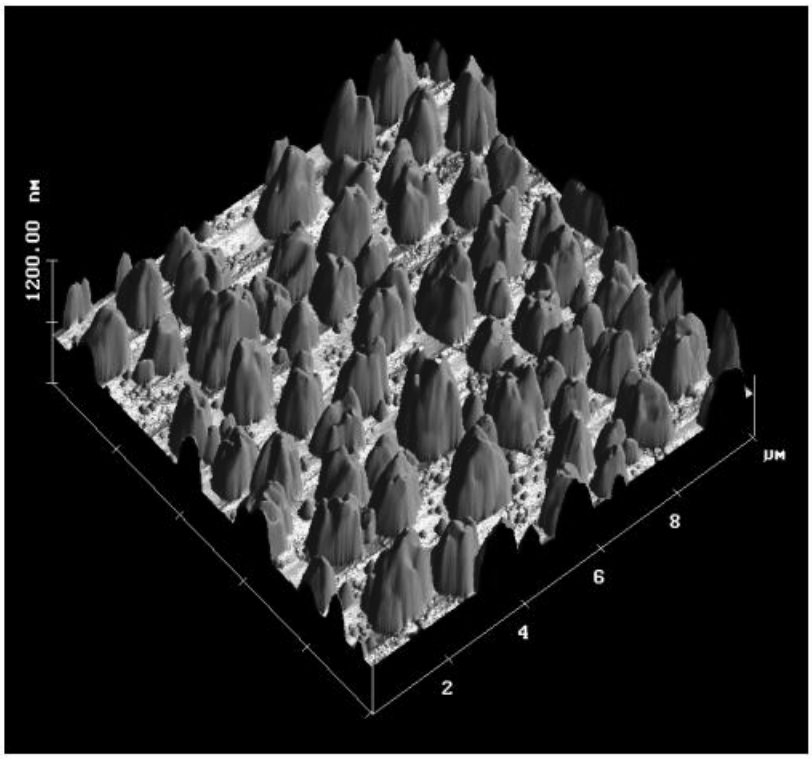

Fig. 1

Fig. 1. AFM image of a Pd film annealed in oxygen at 900^{o}C showing ~ 1µm high uniformly spaced tips.

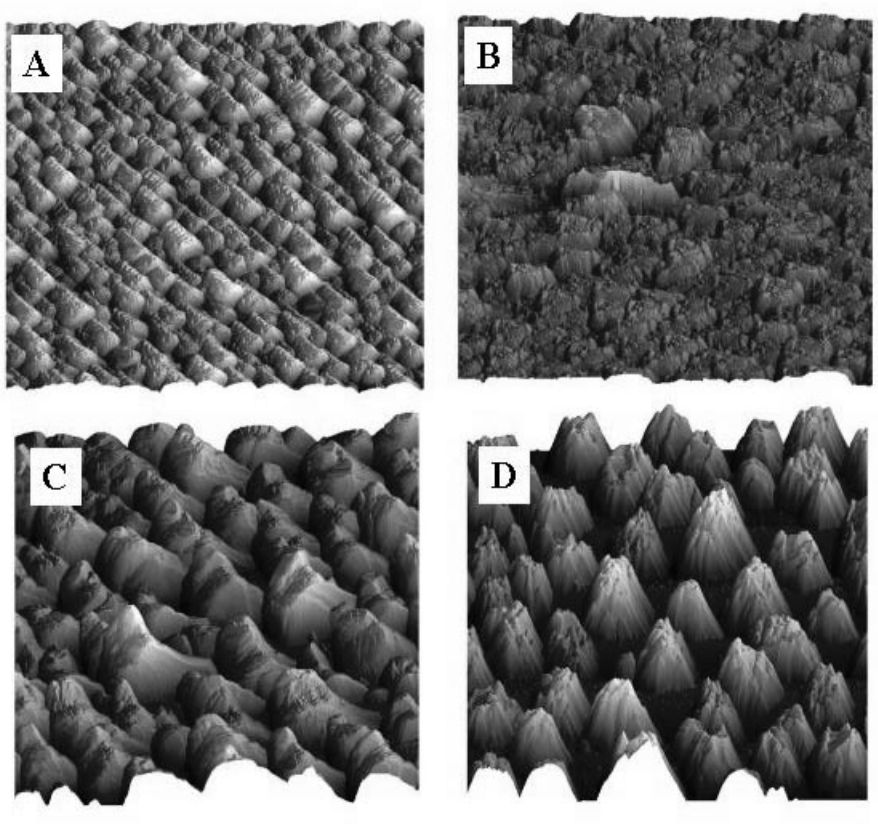

Fig. 2

Fig. 2. AFM images (10 by 10 μm; z-range: 1.4μm) of Pd films of varying crystallinity and annealing ambient at 900°C for 1hour: (A) epitaxial film annealed in vacuum, (B) epitaxial film annealed in oxygen, (C) polycrystalline film annealed in vacuum, and (D) Polycrystalline film annealed in oxygen.

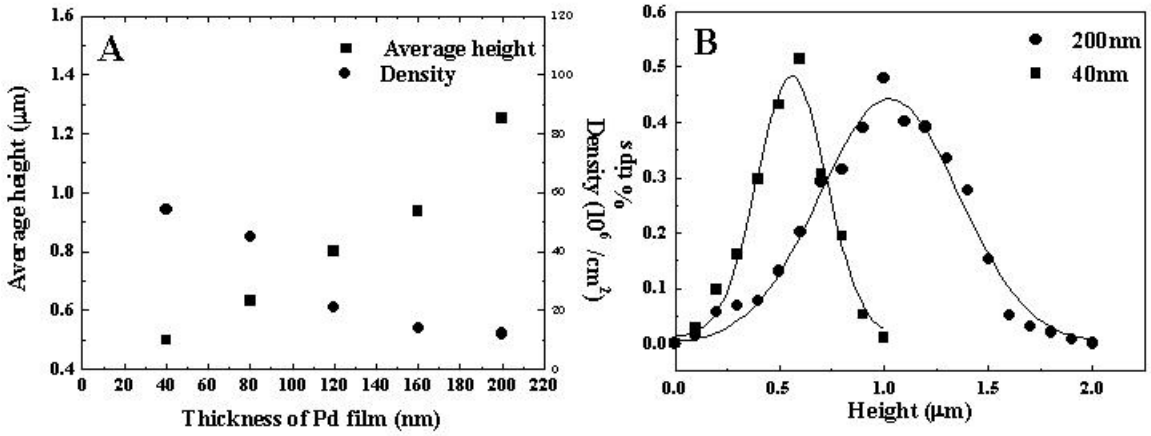

Fig. 3

Fig. 3. (A) Average height and density of the tips plotted as a function of Pd film thickness. (B) The height distribution for the thickest and thinnest film.

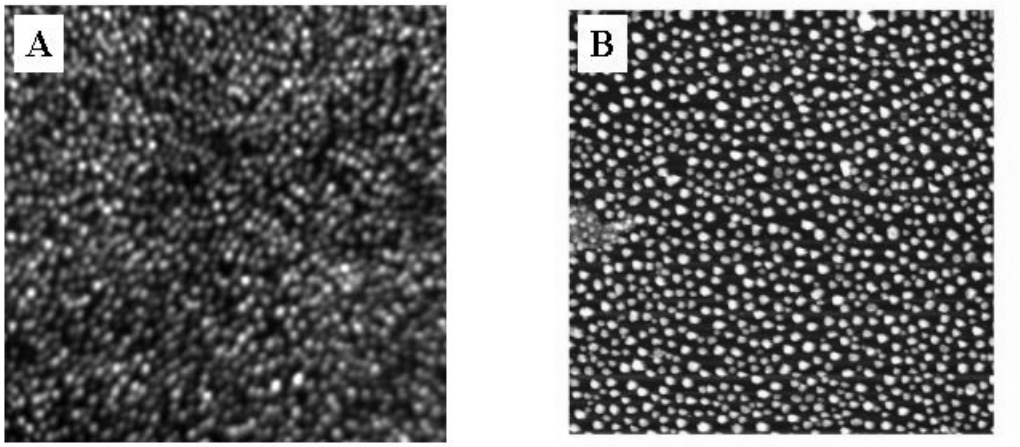

Fig. 4

Fig. 4. (A) PEEM image and (B) AFM image (50 by 50 μm) of a 80nm thick Pd film annealed in oxygen at 900°C for 1 hour.