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Formation and field emission characteristics of nitrogen plasma-treated titanium dioxide clusters

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ABSTRACT

Nitrogen plasma treatment was used to enhance the field emission (FE) properties of titanium dioxide (TiO_2) clusters and form nitrogen doped TiO_2 (N-doped TiO_2) on the TiO_2 clusters. The TiO_2 clusters were grown directly onto the Fe/Al/Ti sheet using atmospheric annealing. The N-doped TiO_2 content was controlled using the nitrogen plasma treatment time. Because continuous nitrogen plasma treatment damages the N-doped TiO_2/TiO_2 cluster surface, increasing the N-doped TiO_2 content could not continually improve the FE current density. A balance between the N-doped TiO_2 content and surface damage must be reached to attain a relatively higher FE current density. The FE characteristics are discussed with regard to the N-doped TiO_2 content and the cluster surface morphologies. An optimal nitrogen plasma treatment time of 60 min was developed in this study to attain the highest FE current density.

1. Introduction

Considerable works have been dedicated to titanium dioxide (TiO_2) related materials in recent years. The special physical and chemical properties of TiO_2 related materials have been investigated for developing a variety of nano-compound materials, nano-devices and nano-systems. TiO_2 with diverse structures, low cost, nontoxicity, chemical and thermal stability properties, has been widely used in many application fields, such as solar cells, [1,2] gas sensors [3,4], electrochemical electrodes [5] and field emission (FE) displays [6,7]. Two crucial Fowler–Nordheim (FN) relation factors determine FE performance: [8] the surface enhancement factor (β) and work function (ϕ). Some approaches, such as modifying the TiO_2 shapes into nanotubes [9] and needles [10], were exploited to increase the β in order to improve the FE current density. Using lowered ϕ, such as doping impurities into the TiO_2 [11–13] and nitrogen doped TiO_2 (N-doped TiO_2) formation onto the TiO_2 surface were effective methods for enhancing FE current density [14].

N-doped TiO_2 exhibits a relatively low energy band gap than that of pure TiO_2 for electrons to emit from the Fermi level into vacuum [12,15,16]. In addition, N-doped TiO_2 has a more stable FE characteristic than TiO_2 [14], making it a promising material for FE applications [17]. N-doped TiO_2 can be synthesized directly by sputtering with a TiO_2 target in nitrogen plasma treatment [18]. It has been reported that TiO_2 could be thermally converted into N-doped TiO_2 using rapid thermal nitridation in a NH_3 environment [19]. This result allows TiO_2 to be used as a template with the N-doped TiO_2 formed onto the TiO_2 surface as an emitter.

We directly grew TiO_2 clusters onto Fe/Al/Ti samples by annealing in atmosphere. The nitrogen plasma treatment was used to form N-doped TiO_2 onto the TiO_2 surface. The N-doped TiO_2 content increased with the increase in nitrogen plasma treatment time. Because the continuous nitrogen plasma treatment damaged the N-doped TiO_2/TiO_2 cluster surface, increasing the N-doped TiO_2 content could not continuously improve the FE current density. The FE characteristics will be discussed with regard to the N-doped TiO_2 content and the cluster surface morphologies.

2. Experimental

Ti sheets $10 \times 10\ mm^2$ in size were used as the substrate. Number 1200 sandpaper was used to polish the Ti sheet surface. After depositing Al(5 nm) and Fe(3 nm) thin films sequentially onto the Ti sheets using e-beam evaporation, the Fe/Al/Ti samples were placed into a quartz tube with a diameter of 50.8 mm. The quartz tube was then placed horizontally inside a furnace. The

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Fe/Al/Ti samples were annealed at a temperature of 900 °C in atmosphere for 60 min. At 900 °C, the Fe film would change into small particles [20]. The Al film was used as the buffer layer for the uniform distribution of Fe particles. According to our experimental result, after annealing, it is obvious that there is a clear boundary in the near middle region as shown in the following scanning electron microscopy (SEM) image (Fig. 1). In the SEM image, the Fe/Al films were pre-coated onto the left-hand side part and no films were pre-coated on the right-hand side part. After annealing, the TiO_2 clusters were only formed on the left-hand side part. Therefore, the Fe particle may be used as a nucleus for TiO_2 cluster formation. After cooling to room temperature TiO_2 clusters were formed onto the Fe/Al/Ti sheets resulting from the combination of Ti and oxygen in the atmosphere. To improve the TiO_2 FE characteristics of TiO_2 the synthesized TiO_2 clusters grown onto the Fe/Al/Ti sheets were transferred to another vacuum chamber for nitrogen plasma treatment to form N-doped TiO_2 onto the TiO_2 clusters. Fig. 2 shows a schematic drawing of the nitrogen plasma treatment equipment. The equipment was an RF magnetron sputtering system. The TiO_2 samples were placed in the target part of the RF magnetron sputtering chamber. The target part diameter was 50 mm and covered with a stainless holder to prevent the carbon target from sputtering. According to the RF magnetron sputtering principle, this design could confirm the nitrogen ions bombard the TiO_2 samples directly. In the general situation, if the TiO_2 samples were not biased then the nitrogen ion energy was too low to dope into the TiO_2. The nitrogen plasma was produced using an RF generator with a power of 25 W at a pressure of 2×10^{-2} Torr. The nitrogen plasma treatment time was set as the parameter for adjusting the N-doped TiO_2 content in the TiO_2 clusters.

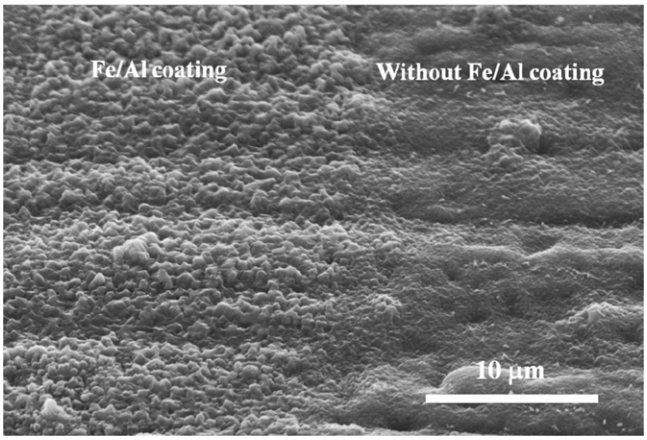

Fig. 1. The different morphology of TiO_2 between coating and non-coating Fe/Al films.

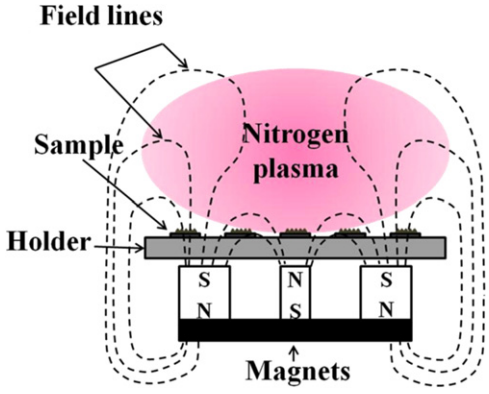

Fig. 2. Schematic illustration of the nitrogen plasma treatment equipment.

SEM was used to observe the surface morphology of the synthesized clusters. X-ray photoelectron spectroscopy (XPS) was performed to study the composition of the samples. The microstructural information was examined using Raman spectroscope with an Ar laser exhibiting an excitation wavelength of 514.5 nm. The FE measurement was carried out with a homemade apparatus consisting of a pair of parallel plates, conducted in a high-vacuum environment with a pressure of about 5×10^{-7} Torr. The distance between the cathode (sample) and the anode (stainless plate) was 125 μm. The FE measured sample size was 8×8 mm^2.

3. Results and discussion

Fig. 3(a) shows a SEM image of the synthesized TiO_2 clusters grown onto the Fe/Al/Ti sheet. The inset of Fig. 3(a) shows the magnified SEM image of the TiO_2 cluster. The surface morphology of the TiO_2 clusters exhibited a knoll shape with a size of about $3 \times 3 \times 3$ μm^3 and a number density of about 2.5×10^8 cm^{-2}. The simple method used to anneal the Fe/Al/Ti sheet provided effective uniform large-area TiO_2 cluster growth. To enhance the FE current density the nitrogen plasma treatment was performed to form the N-doped TiO_2 onto the TiO_2 clusters. The nitrogen plasma treatment time was used to adjust the N-doped TiO_2 content in the TiO_2 clusters. Fig. 3(b)–(f) are SEM images of the TiO_2 clusters treated with treatment times of 15, 30, 45, 60, and 75 min, respectively. According to the SEM images the surface morphologies including the size, number density and distribution uniformity, with nitrogen plasma treatment times of 15, 30, and 45, were slightly changed from the pristine TiO_2 clusters. When the nitrogen plasma treatment time was 60 min, due to long continuous nitrogen ion bombardments, TiO_2 cluster surface damage was produced. Moreover, when the nitrogen plasma treatment time reached 75 min, the TiO_2 cluster surface suffered more damage and presented a relatively smoother morphology.

Fig. 4 shows the corresponding Raman spectra of the pristine TiO_2 clusters and revealed four peaks of 240, 440, 609 and 825 cm^{-1}, which indicated that the clusters were composed of a TiO_2 rutile structure [21]. The normalized Raman spectra show that after nitrogen plasma treatment the TiN peak (320 cm^{-1}) appeared. However the TiN peak intensity did not increase with nitrogen plasma treatment time [22]. With the nitrogen plasma treatment time increasing, the Raman spectra of the N-doped TiO_2/TiO_2 cluster surface shows that no anatase peaks can be found [23]. Therefore, the N-doped TiO_2 content was examined by XPS to observe the surface composition. Before the XPS measurements the binding energy data was calibrated with the C 1 s signal at 284.6 eV. According to the XPS results, Fig. 5(a) shows the pristine TiO_2 clusters had peaks of TiO_2 compounds of 458.8 and 464.7 eV [24]. With increasing nitrogen plasma treatment time, the TiO_2 peaks gradually presented non-symmetrical shoulders. By fitting these non-symmetrical shoulders, Figs. 5(b)–6(f) obtained a peak centered at 457.1 and 463.0 eV, which represents the N-doped TiO_2 signals [25,26]. The N-doped TiO_2 peak intensity increased when the nitrogen plasma treatment time was increased. The N-doped TiO_2 content could be increased to about 51.2 at% after 75 min nitrogen plasma treatment.

Fig. 6(a) shows the FE current density versus applied electric field characteristics for the TiO_2 clusters with different nitrogen plasma treatment times. In Fig. 6(a) the pristine TiO_2 clusters with rutile structure did not demonstrate noticeable FE current density. This result coincides with the previous reports [27,28]. In samples treated with nitrogen plasma, it is obvious that as the