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Thermal dewetting of Pt thin film: Etch-masks for the fabrication of semiconductor nanostructures

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Abstract

Nanometer scale Pt metal islands formed by the dewetting of two-dimensional film on SiO_2 dielectric materials during rapid thermal annealing were investigated. For the case of 30 nm thick Pt films, pattern formation and dewetting were initiated at temperatures of >600 °C. Controlling the annealing temperature and time as well as the thickness of the Pt metal film permitted the size and density of Pt islands to be controlled. Furthermore, the islands show good resistance to dry-etching by a CF_4-based plasma for dielectric etching, indicating that the metal islands produced by dewetting are suitable for use as an etch-mask in the fabrication of nano-scale structures.

Keywords: Nanostructure; Dewetting; Pt; GaN; Thermal annealing

1. Introduction

Low-dimensional semiconductor nanostructures have considerable potential for use in applications in optoelectronic devices such as low-dimensional laser diode and waveguide using a photonic band gap [1]. The bottom-up method which is generally achieved by the precise control of growth by exploiting a self-assembly technique, has the advantage that is free from the possible damage caused by dry-etching, but has a drawback, in that it is difficult to arrange and to control the dimensions [2]. In comparison, the top-down method which generally involves electron-beam lithography integrated with a dry-etching technique [3] to produce a nanostructure, has the advantage of controllability of the pattern size and the arrangement of the structure. However, the electron-beam lithographic method has critical disadvantages, such as the low throughput and high equipment costs [4].

On the one hand, some researchers have investigated alternative methods that avoid the use of electron-beam lithography for reliable pattern formation, especially for a suitable mask for the dry-etch. These approaches are the use small colloid particles [5] or small aerosol particles [6]. However, these masks have critical problems, such as a low-resistance against dry-etching, especially for GaN and related materials which have a high bind strength. On the other hand, the dewetting of metastable thin metal films on a solid substrate is currently a topic of great interest, due to applicational relevance, e.g., in thin film technology [7]. Two-dimensional metal films deposited on dielectric substrates are typically thermodynamically unstable and, when heated, become rough as the result of dewetting [8]: if the surface energy of the metal film γ_m is greater than the sum of the interfacial energy and surface energy of the underlying substrate, then agglomeration of metal islands with a finite contact angle between the film and substrate is energetically favored and the film can undergo dewetting at elevated temperatures [9]. Dewetting of an initially two-dimensional film can occur via heterogeneous nucleation and growth, or via spinodal dewetting, in which thermal fluctuations of a critical wavelength grow exponentially [10].

In this paper, we report findings to show that the thermal annealing of Pt films can induce dewetting of the film with a high density of nanometer scale islands appearing on the dielectric surface. Furthermore, a method for the fabrication of a nano-scale GaN structure by inductively coupled plasma etching is also proposed, in which the Pt clusters are utilized by dewetting of the two-dimensional Pt film on the SiO_2 as etch-masks.

2. Experimental

The experimental procedure used in this study is shown in Fig. 1. Undoped GaN samples, with a thickness of 1 μm, were

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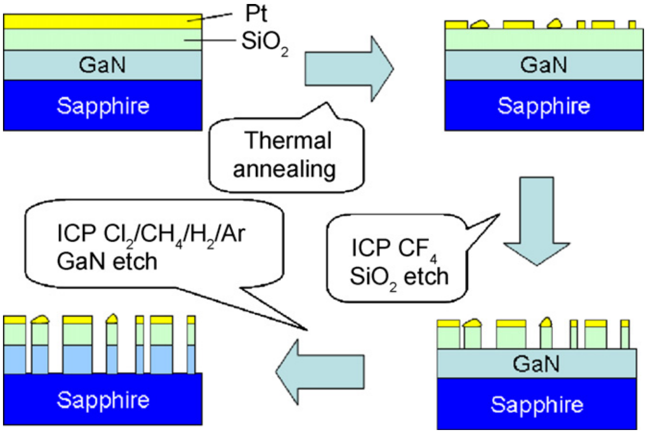

Fig. 1. Experimental procedure with the process sequence.

grown on a sapphire substrate (c-plane) in a metal organic chemical vapor deposition system using trimethylgallium (TMGa) and NH_3 as the precursors. The samples were transferred immediately after the GaN growth into the plasma enhanced chemical vapor deposition system and the SiO_2 dielectric materials, with a thickness of 0.5 μm, were then grown on the GaN surface using SiH_4 and N_2O as source gases under 1 Torr chamber working pressure. Pt thin films with thicknesses of 3, 15, and 30 nm were, subsequently deposited on the SiO_2 surface, respectively, in the electron-beam evaporation chamber.

The samples were heated from 500 to 1173 K in a conventional rapid thermal annealing system (RTA) and the annealing time was also varied from 1 to 6 min under a N_2 atmosphere in order to investigate the thermodynamic characteristics of metal dewetting. The typical annealing process consists of four steps, pre-heating-step (423 K), ramping-up-step (3 K/s), steady-step, and finish-step. The surfaces of the samples were examined by

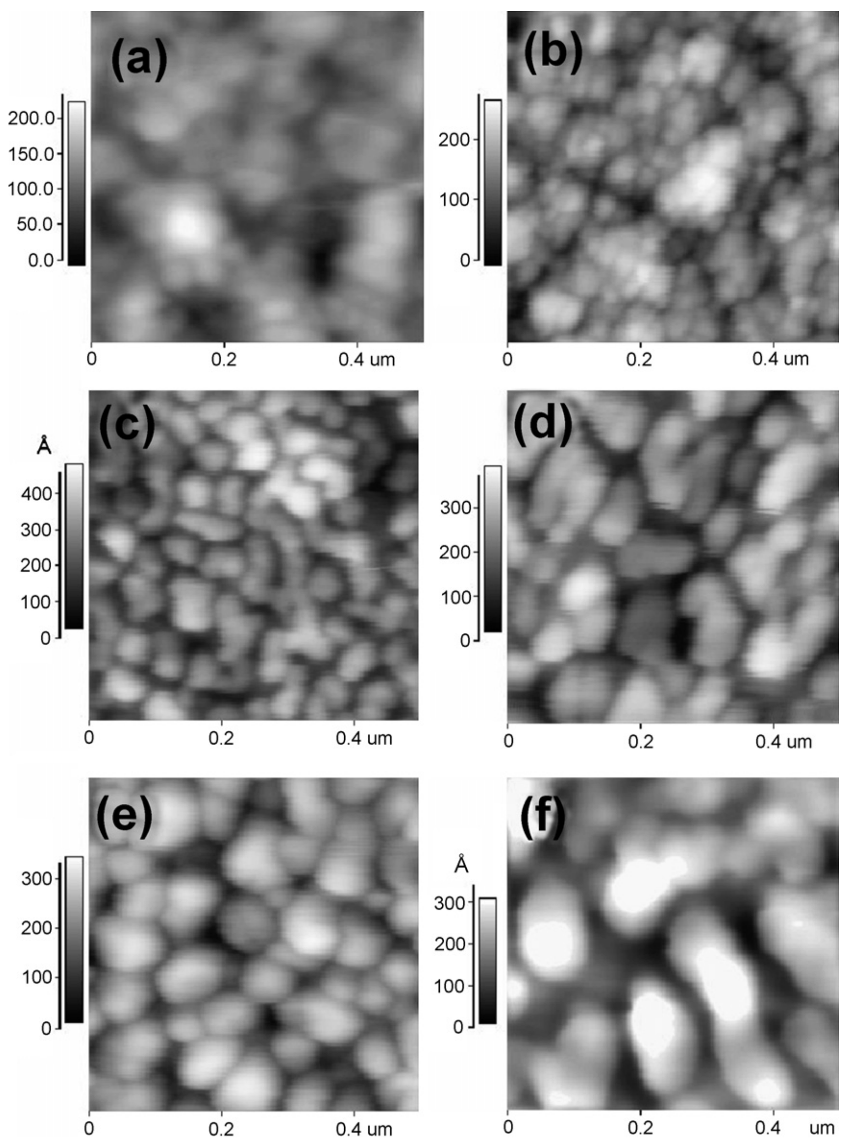

Fig. 2. Surface morphologies of Pt (3 nm) on SiO_2 for (a) as-deposited and annealed samples at temperatures of (b) 500 K, (c) 573 K, (d) 673 K, (e) 773 K for 1 min, and (f) 773 K for 3 min.

atomic-force microscopy (AFM) before and after the annealing, the SiO_2 etching, and the GaN etching, respectively.

In order to investigate the feasibility of using Pt islands as etch-masks, the dry-etching of a SiO_2 film was conducted in the inductively coupled plasma (ICP) system using CF_4-based plasma chemistry. Subsequently, the underlying GaN films were also etched with a $Cl_2/CH_4/H_2/Ar$ plasma as etchant gases by using Pt/SiO_2 as the etch-mask. The etch conditions used for GaN were: 30 Standard Cubic Centimeter per Minute (SCCM) Cl_2, 8 SCCM H_2, 16 SCCM Ar, 1.3 Pa pressure, 1500 W ICP power, 150 W rf power, and a 20 °C table temperature. A detailed descriptions of etch conditions used here can be found in Ref. [11].

3. Results and discussion

Fig. 2 shows AFM images of the surface morphologies of Pt (3 nm) on SiO_2 for (a) as-deposited and annealed at temperatures of (b) 500 K, (c) 573 K, (d) 673 K, (e) 773 K for 1 min, and (f) 773 K for 3 min. For annealing at temperatures less than 500 K, the morphologies were essentially featureless with slight roughness, identical to an as-deposited film. At a temperature of 500 K, the morphology of two-dimensional Pt films starts to become rough and the roughness value of the film, as measured by AFM, was significantly increased. As the temperature was increased to 573 K, the two-dimensional film begins to dewet and a partially connected patterned structure appears with a drastically increase in film roughness, as shown in Fig. 2(c). It is noteworthy that the surface energies of the Pt film is about 1800 mN/m [12], which is much higher than those of SiO_2 film [13], indicating that the Pt film is unstable on SiO_2 dielectric materials, resulting in the dewetting of the film.

At a higher temperature of 673 K, as shown in Fig. 2(d), the Pt islands assume a more circular shape, indicating that the Pt atoms rearrange by themselves, to achieve an energetically stable state by decreasing the surface free energy. At 773 K, the dewetting process is nearly finished and a large fraction of the substrate area is exposed. The average height, width, and

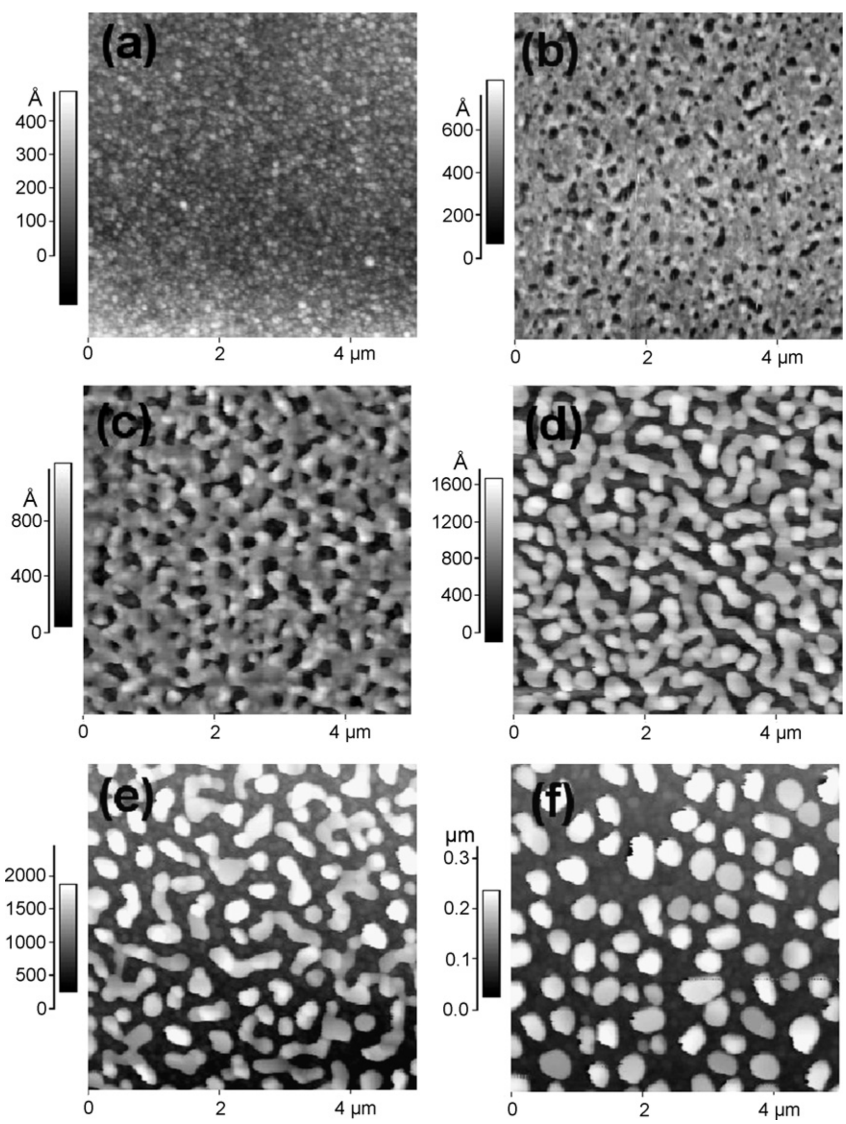

Fig. 3. Surface morphologies of Pt (30 nm) on SiO_2 for (a) as-deposited and annealed samples at temperatures of (b) 873 K, (c) 973 K, (d) 1073 K, (e) 1173 K for 1 min, and (f) 1173 K for 3 min.

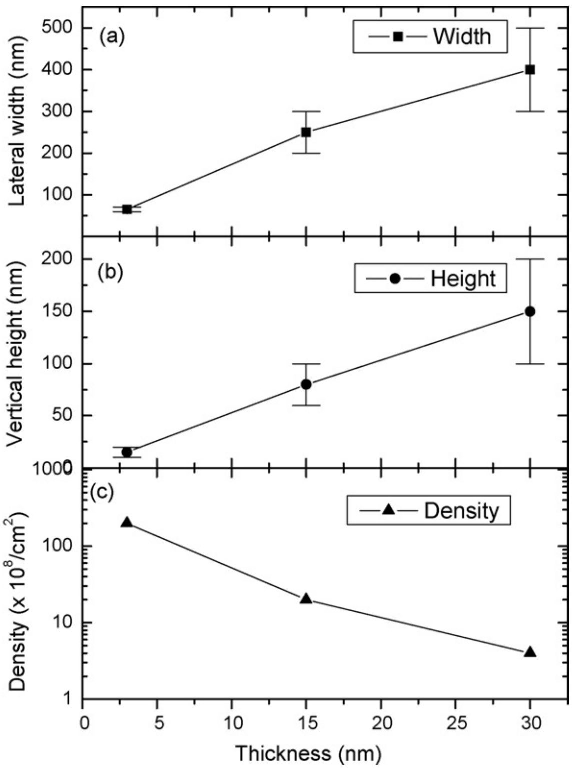

Fig. 4. (a) Lateral width, (b) vertical height, and (c) total density of dewetted Pt islands as determined from the AFM images.

density of the Pt islands were determined to be about 20 nm, 60 nm, 2×10^{10} cm^{-2}, respectively. Hu et al. [8] reported on the formation of nano-scale patterns for dewetted Pt by ion-beam irradiation showing the lateral patterns sizes of 8–30 nm. Compared to these results, the lateral sizes of patterns in our sample are larger than those of Hu, since ion-beam irradiation should be accompanied by the physical removal of the Pt from the surface. Even though evaporation of Pt atoms from the surface by annealing is possible, the overall rate of evaporation should be negligible due to the low vapor pressure of Pt, which is characteristic of noble metals.

When the sampled was annealed at 773 K for 3 min, however, the coalescence of islands due to the mass-transfer of atoms in the surface of islands was observed as shown in Fig. 2(f), and as a result, the overall size of the islands was increased.

Fig. 3 shows AFM images of the surface morphologies of as-deposited and annealed Pt (30 nm) film on SiO_2. For temperatures of less than 873 K, the morphologies are nearly identical to the surface of an as-deposited film (Fig. 3(a)), as in the case of the previous results. At annealing temperature over 873 K, the surface morphologies change in a distinctive manner. For the thinner Pt films, as shown in Fig. 2(c), the Pt is isolated and surrounded by holes or craters, while the holes are somewhat interconnected. On the contrary, the holes or craters are isolated and surrounded by the Pt, while the Pt areas are interconnected (seen in Fig. 3(b)). Such Swiss-cheese-like morphologies formed on thicker Pt films as the result of dewetting were also observed by Hu et al. [14] by using ion-beam irradiation method. This shows that the dewetting mode of 30 nm Pt films is different from that for thin (3, 15 nm) Pt films.

As the temperature is increased to 973 K, the holes become increasingly large. Eventually, the large holes become interconnected at temperatures of 1073 K and Pt is completely isolated and surrounded by holes at 1173 K. When the sampled was annealed at 1173 K for 3 min, the size of the Pt islands was reduced and the uniformity of the lateral size was enhanced, as shown in Fig. 3(f). In comparison with the results for Pt films with a thickness of 3 nm, the coalescence did not occur in this

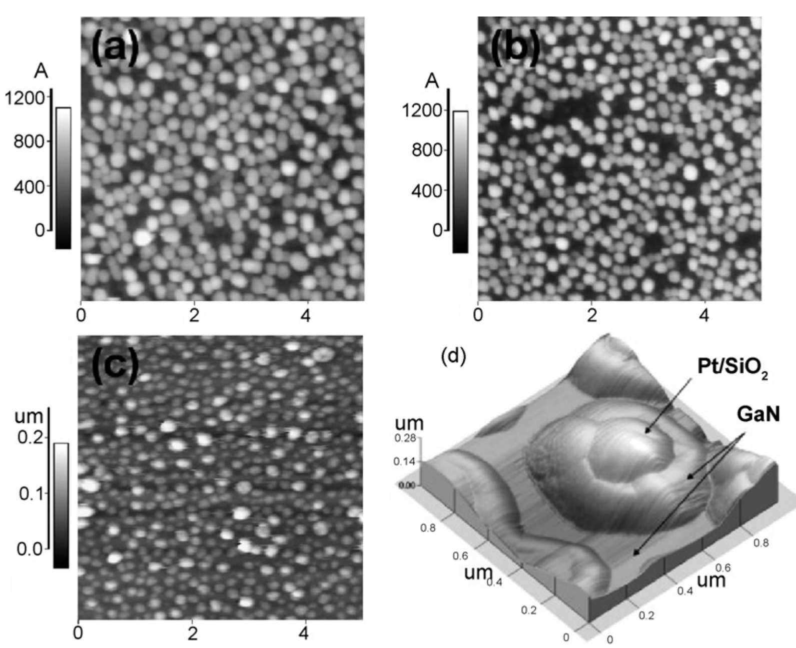

Fig. 5. AFM images of Pt (15 nm)/SiO_2 (0.3 μm) (a) annealed at 973 K for 3 min, (b) etched by a CF_4 plasma for SiO_2 patterning, and (c) etched by a $Cl_2/CH_4/H_2/Ar$ plasma for GaN pattering. (d) Magnified 3D-view of an etched surface of Pt (30 nm)/SiO_2 (50 nm)/GaN. The depth of the etched GaN is about ∼0.15 μm.

sample, but rather, the separation of the islands was observed resulting in the reduction in size dispersion. The exact origin of the change in dewetting mode as well as the reduction in size dispersion with increasing thickness and annealing time is currently under investigation.

Fig. 4 shows the lateral width, vertical height, and density of Pt islands as a function of film thickness. As shown in Fig. 4(a) and (b), the width and height of the Pt islands increased with increasing thickness by 6.5 and 7.5 times, respectively. The density of Pt islands was decreased, as expected, by an order of magnitude from $2 \times 10^{10}\,cm^{-2}$ for 3 nm to $2 \times 10^{8}\,cm^{-2}$ for 30 nm film, due to the increased dimensions of the dewetted Pt islands.

Fig. 5 shows the sequence used in fabricating GaN nanostructures using dewetted Pt islands as etch-masks. The surface morphology after CF_4 plasmas etching, shown in Fig. 5(b) is essentially identical to that of an as-annealed film (Fig. 5(a)), indicating that the metal islands produced by dewetting are suitable for use as an etch-mask. Subsequently, the GaN is etched without exposing the sample to the atmosphere. As can be seen in Fig. 5(c), the etched surface morphology was similar to that of an as-annealed and SiO_2-etched surface, indicating that the patterns were successfully transferred to the GaN surface. The etch-anisotropy, as shown in Fig. 5(d) was deteriorated somewhat by the $Cl_2/CH_4/H_2/Ar$ plasma due to the erosion of mask-edge arising from the high density of energetic ions in the plasma. The etch properties could be enhanced by optimizing the current etching procedure used in this study.

4. Conclusion

Nano-scale Pt metal islands were formed by the dewetting of two-dimensional film on SiO_2 dielectric materials during a rapid thermal annealing process. The initiation of pattern formation by the dewetting process is closely related to the thickness of film and the annealing temperature. The precise control of the annealing temperature and time as well as the thickness of Pt metal film permitted the size and density of the Pt islands to be controlled. The islands show good resistance against dry-etching when a CF_4-based plasma is used in the dielectric etching. This fabrication method was also proven to be effective in the fabrication of GaN nanocolumns.

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