Materials Science in Semiconductor Processing 16 (2013) 160–164

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Long-range-ordered Ag nanodot arrays grown on GaAs substrate using nanoporous alumina mask

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ARTICLE INFO

Available online 1 June 2012

Keywords:
Porous anodic alumina
GaAs
Ag nanodot arrays

ABSTRACT

With more and more attention given to the plasmonic nanostructures enhancing light trapping of solar cells, the fabrication of metal nanostructures becomes more and more important. In this work, we fabricated porous anodic alumina on SiO_2/GaAs substrate and obtained periodic Ag nanodots with hemispherical shape by electron beam evaporation. During the experiments, it was found that the properties of barrier layers of porous anodic alumina fabricated on SiO_2/GaAs and SiO_2/Si substrates after pore-widening are different. The through-hole porous anodic alumina film on SiO_2/GaAs substrate cannot be obtained after a long pore-widening process. The additional Ar ion bombardment against the samples was needed in our experiments to get the through-hole porous anodic alumina films on SiO_2/GaAs substrate.

1. Introduction

The plasmonic nanostructures enhancing light trapping of solar cells recently has been given more and more attention owing to the unique characteristics of surface plasmon polaritons (SPP) [1–7]. So the fabrication of metal nanostructures is very important when using plasmonic nanostructures to enhance the light trapping of solar cells. There are many methods to fabricate periodic metal nanostructures including electron beam lithography [8] and focused ion beam [9]. However, the low throughput and high cost of them lead to limited applicability for the fabrication of nanopatterns with large coverage area.

As a well known nano-template, porous anodic alumina masks (PAAMs) have been intensively studied [10–14]. They are simple, inexpensive, lithography-free, and have highly ordered and controllable structures as well as good chemical and thermal stability [14]. In 1996, Masuda and Satoh fabricated Au nanodot arrays using porous anodic alumina (PAA) as an evaporation mask for the first time [10]. In their work, they developed a two-step anodizing process which could result in a thin PAA mask with an ordered through-hole array. This PAA mask is applicable as the mask of evaporation. After that, many works on fabricating nanodot arrays of various metals have been conducted using PAA film as an evaporation mask [15–19]. However, the reports about PAAMs used on GaAs substrates are very few especially for fabricating PAA directly on GaAs substrates [20–22]. Almost all of the reports about using PAAMs to fabricate nanodots on GaAs substrates are fulfilled by binding the PAAMs on the GaAs substrates [23–25]. One big problem of this process is the poor adhesion between the PAA mask and the substrate.

In this work, we fabricated PAA template on SiO_2/GaAs substrate and obtained periodic Ag nanodots with hemispherical shape by electron beam evaporation (EBE). Here, the SiO_2 layer is used to protect GaAs substrate [26].

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http://dx.doi.org/10.1016/j.mssp.2012.05.008

The advantage of this procedure is that the technological processes necessary to fix the alumina mask on top of GaAs are suppressed and consequently the related GaAs surface contamination is avoided. Moreover, this work provides a good foreshadow of further research on fabricating periodic metal nanodots on GaAs solar cells to study the SPP effects.

2. Experiments

The starting substrates in this study are clean GaAs (100) wafers with $0.58–3.15 \times 10^{18}\ cm^{-3}$ carrier concentration and $1.25–4.79 \times 10^{-3}\ \Omega\,cm$ resistivity. Then highly pure aluminum (99.99%) layers with thickness of 1500 nm were evaporated on them. The deposition of aluminum was done using EBE at a rate of 0.2–0.5 nm/s and a pressure of 2.9×10^{-4} Pa. Before the aluminum was evaporated, thin film SiO_2 layers with thicknesses of 50 nm and 200 nm were evaporated on front and back of the GaAs substrates respectively using ion beam sputtering. The SiO_2 layer was used as a protective layer. Then the prepared samples were cleaned ultrasonically for several minutes in alternate baths of acetone and alcohol, rinsed several times with deionized water and blown dry with nitrogen gas. The anodization was performed using 0.3 M oxalic acid maintained at 15 °C. A gold sheet was used as the cathode and the anode was connected with aluminum on SiO_2/GaAs substrate directly. A circular area of 1 cm diameter aluminum on the SiO_2/GaAs substrate was exposed to electrolytic solution in an insulated bath while the electrolyte was mechanically stirred. The first anodization was done at a constant dc voltage of 40 V for 15 min 30 s. Because the growth rate of the PAA depends on several operating parameters, we determined the first anodization time by an empirical method to obtain the final PAA template with a height of ~250 nm. Then the first anodized layer was etched in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C for 7 min 20 s. A second anodization was performed under the identical conditions as the first anodization step and carried out until the current of circuit dropped significantly. To ensure complete conversion of the entire aluminum into its oxide, the voltage was maintained for 60 s after the current had stabilized at a low value. To enlarge the pore size and remove the anodic alumina barrier layers at the bottoms of the pores, the anodized samples were immersed in phosphoric acid solution (5 wt%) at 30 °C for 32 min after the second anodization. In order to further obtain the through-hole PAA films, the Ar ions bombardment process by an inductively coupled plasma (ICP) dry etcher was needed. The time of bombardment was about 40 s with an argon flow rate of 40 sccm.

After the fabrication of the through-hole PAA mask on SiO_2/GaAs substrates, a 30-nm-thick Ag layer was deposited on the samples by EBE at a rate of 0.6 Å/s at 10^{-6} Torr. Then, the PAAMs were removed by simply immersing the samples in 1 M NaOH solution for several minutes followed by a rinse with deionized water. Finally, the highly ordered Ag nanodot arrays were left on the surface of the SiO_2/GaAs substrates. In order to make the steps of fabrication more visual, Fig. 1 shows the whole experimental processes.

Structures of the fabricated PAA masks and Ag nanoparticle arrays were observed using a scanning electron microscope (SEM). The size distributions of the PAA pores and Ag nanoparticle arrays were determined using the ImageJ analysis software on SEM images [27].

3. Results and discussion

The typical surface and cross-section morphology of the prepared PAA mask after pore-widening on SiO_2/GaAs substrate are presented in Fig. 2. These images apparently

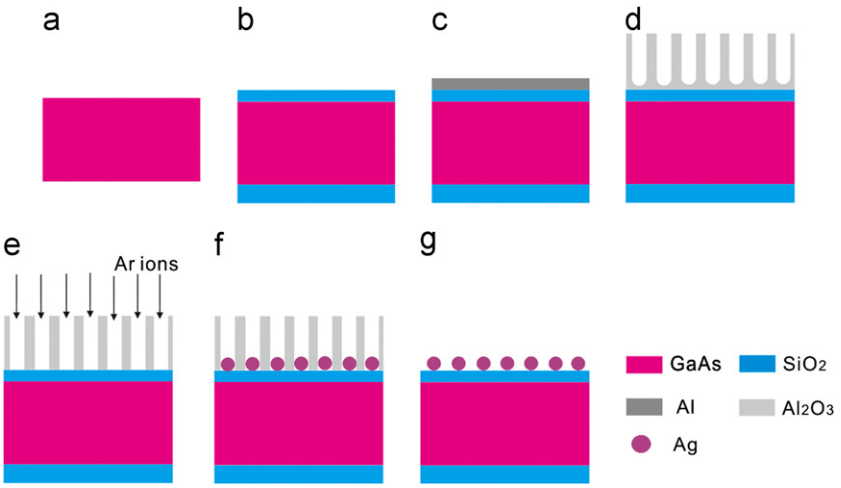

Fig. 1. Schematic diagram of the whole experimental processes to fabricate nanodot arrays on SiO_2/GaAs surface: (a) GaAs substrate is prepared; (b) SiO_2 layers with thickness of 50 nm and 200 nm are separately evaporated on the front and back surface of GaAs substrate by ion beam sputtering; (c) an aluminum film with 1500 nm thickness is evaporated by EBE; (d) an alumina mask is created on the GaAs substrate using a two-step anodization process and a pore-widening process; (e) sample is bombarded by Ar ion to get the through-hole PAA film; (f) Ag material is deposited into the PAA pores and (g) PAA template is removed and a silver nanodot array remains on the GaAs substrate.