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Fabrication of highly aligned nano-hole/trench structures by atomic force microscopy tip-induced oxidation and atomic hydrogen cleaning

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Abstract

We fabricated highly aligned nano-hole and trench structures on GaAs (001) by a combination of atomic force microscope (AFM) tip-induced oxidation and atomic hydrogen etching. Highly aligned oxide dot and line structures at the nano-meter scale were patterned by using AFM tip-induced oxidation. Then, the oxide structures and surface oxides were removed by using atomic hydrogen. Finally, nano-hole and trench structures with atomically flat surface were successfully achieved. The smallest hole diameter obtained in the present work was 13.4 nm with the depth of 0.47 nm. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Hydrogen has quite a large number of application fields in semiconductor processes [1–8]. Atomic hydrogen is also very interesting element in semiconductors because it is able to be applied to surface cleaning [1–4], band gap tuning [5], hydrogenation [6], wafer bonding [3], hydrogen-assisted crystal growing [7], and passivation [8] in semiconductor processes. Many researchers have confirmed that atomic hydrogen induces surface cleaning to get a high-quality epilayer during

initial growth stage and atomically flat semiconductor surface for further application [1–8].

Recently, there have been many proposals for nano-structures in device applications and physical models, such as quantum coupling, quantum dot cellular automata, and quantum computation [9,10]. In particular, for the application of the quantum devices, it is necessary to fabricate site-controlled and highly aligned artificial nano-structures. In the past several years, the demands for site-controlled and highly aligned artificial nano-structure fabrication are increasing. Many research works for the fabrication of site-controlled nano-structures by artificial techniques have been reported by using electron-beam

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lithograph [11], scanning tunneling microscope (STM) tip-assisted patterning [12], and atomic force microscope (AFM) tip-induced oxide patterning [13–17]. A number of works demonstrated that an AFM could be used for the oxidation on semiconductors and metal films [13–18].

In particular, the fabrication of nano-hole and trench structures can be an important technique for the site-controlled quantum nano-structures based on the control of atomic migration [11,12,19]. Nano-hole structures were introduced by depositing a thin GaAs layer on STM tip-assisted patterning on GaAs (001) substrate [12], electron-beam lithography combined with Cl_2 gas etching on GaAs [11], and locally strain-enhanced etching of a GaAs cap layer grown on an InAs QD layer [19]. Nano-trench structures were also fabricated by AFM tip-induced oxidation based on NH_4F etching on modified Si (111) [18] and direct patterning on GaAs (100) surface by AFM [20]. In addition, to realize the site-controlled nano-structures based on the migration control of adatoms, the atomically flat surface is also required after the formation of nano-holes and trenches because the atomic migration on surface can be seriously affected by surface roughness.

In this present works, in order to achieve highly aligned nano-hole and trench structures with atomically flat surface, we suggest the novel way of nano-structures fabrication for nano-hole structures using a combination of well-defined AFM tip-induced oxidation and oxide removal on GaAs (001) by atomic hydrogen cleaning.

2. Experimental procedure

First of all, to obtain atomically flat GaAs surface for the process of AFM tip-induced oxidation, GaAs buffer layers were grown with 10-period GaAs/AlGaAs superlattice on Si-doped GaAs (001) substrate. This starting surface flatness was confirmed by high-resolution AFM (Seiko SPA-400).

The starting surface was mounted on programmable site-control AFM (Hitachi SPF-200M) for making oxide structures at the nano-meter scale. Highly aligned nano-meter scale oxide dots and

lines were fabricated on atomically flat GaAs (001) surface by using contact-mode AFM tip-induced oxidation. AFM tip-induced oxidation on GaAs surface was conducted at room temperature under controllable humidity condition. The sizes of oxide structures were controlled by changing the relative humidity, bias voltages and pulse periods (P_P).

In order to remove the oxide structures from GaAs surface, the substrate was transferred into a molecular beam epitaxy (MBE) chamber, where the surface oxide and patterned oxide structures were removed by atomic hydrogen. Atomic hydrogen was generated by molecular hydrogen cracking cell with a tungsten filament [2]. During the surface cleaning, the substrate temperatures were kept below 500°C in order to prevent Ga or As desorption from the surface. The oxide removal from the GaAs surface was confirmed by observation of reflection high-energy electron diffraction (RHEED) pattern. After oxide structures patterning and removing, the surface structures were confirmed by using AFM (Seiko SPA-400).

3. Results and discussion

Fig. 1 shows the schematic illustration of the experimental procedures for the formation of the oxide structures by the AFM (a) and subsequent removal of oxide structures by atomic hydrogen irradiation (b). A very narrow water column can be formed between a tip and a substrate by approaching the tip to substrate. The electrical fields push OH^- in the water column to GaAs surface resulting in the formation of As- and

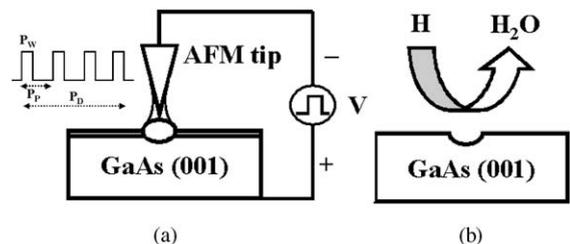


Fig. 1. Schematic illustration for the formation of oxide structures by AFM (a) and removal of the oxide structures by atomic hydrogen cleaning (b).

Ga-oxides. The AFM tip-induced oxide structures are composed of Ga_2O_3 and As_2O_x . During the atomic hydrogen supply, these oxides can be changed to volatile species such as water molecules as well as As_2 , GaOH , and Ga_2O [4,21].

In these works, to achieve various oxide structures with different lateral size and height, the oxidation was carried out by varying the humidity (55–65%), bias voltage (8–12 V), and P_P (10–100 ms) with fixed pulse width ($P_W = 2$ ms) and duration ($P_D = 1$ s). When the relative humidity is below than 50%, it is difficult to oxidize the GaAs surface due to the lack of the water column around the tip [13]. With an increase in the bias voltage, the diameter and height of the oxide dots were increased and the size distribution was also increased (at humidity 55% and $P_P = 20$ ms). Similar results were demonstrated on silicon [14,22], titanium [13], and GaSb [15] surface. At a bias voltage of 8 V and a humidity of 65%, with an increase in the P_P from 10 to 100 ms, which corresponds to zero bias time from 8 to 98 ms, the size uniformity of oxide structures was significantly improved. This can be explained by the fact that space charges in the water column will be neutralized between bias pulses [22]. The oxide lines were also fabricated by varying the bias voltage (5–8 V), humidity (55–65%), and P_P (10–100 ms) with a fixed writing speed of 10 nm/s. From these results, we believe that the highly aligned nano-oxide structures can be easily achieved by using programmable site-control AFM tip-induced oxidation technique under optimized conditions.

In the next stage of the experimental procedures, to keep atomically flat surface and better surface morphology after removing the oxide structures from GaAs surface, the atomic hydrogen cleaning was performed under various cleaning condition, such as substrate temperature ($T_s = 450$ – 500°C), molecular hydrogen flux (1×10^{-6} – 4.7×10^{-6} Torr), molecular hydrogen cracking cell temperature ($T_{cc} = 1200$ – 1400°C), cleaning time (t_c), and with/without As_4 flux (1.2×10^{-5} Torr).

Fig. 2 shows the RHEED patterns for GaAs (001) surface after atomic hydrogen cleaning for 30 min with (a) and without (b) arsenic flux. Without atomic hydrogen irradiation, the

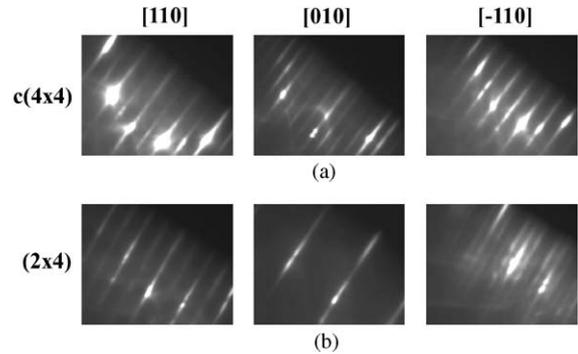


Fig. 2. Typical RHEED patterns taken along the $[1\ 1\ 0]$, $[0\ 1\ 0]$, and $[\bar{1}\ 1\ 0]$ after atomic hydrogen cleaning with (a) and without (b) arsenic conditions.

RHEED pattern showed a halo, to the temperature range from 450°C to 500°C , indicating that an amorphous oxide layer still exists on the surface. The surface was then exposed to atomic hydrogen at different T_s ranging from 450°C to 500°C for 30 min with and without As_4 (1.2×10^{-5} Torr) conditions. A clear RHEED pattern with $c(4 \times 4)$ and (2×4) reconstructions were observed, depending on the arsenic conditions with and without As flux, respectively. Generally, GaAs (001) surface shows a variety of reconstructed structure depending on surface stoichiometry. The structure changes from the most As-rich $c(4 \times 4)$ phase through the 2×4 , 3×1 , and 4×6 phases, and finally to the Ga-rich 4×2 phase as the As coverage is decreased. The reconstructions $c(4 \times 4)$ and (2×4) are As-stabilized surface, which was usually observed on the surface grown under As-rich condition. Therefore, atomic hydrogen effectively removes the surface oxide and contaminants without changing the surface stoichiometry seriously.

Fig. 3 shows tapping mode AFM images for the starting GaAs (001) surface (a), after atomic hydrogen cleaning with (b) and without (c) arsenic supplies. In Fig. 3(a), atomically flat and structure free terraces with atomic steps are clearly observed. In the AFM images for atomic hydrogen cleaning with arsenic supply, two-dimensional structures were appeared on the terraces. On the other hand, for the atomic hydrogen cleaning without arsenic supply, no evidence for the specific

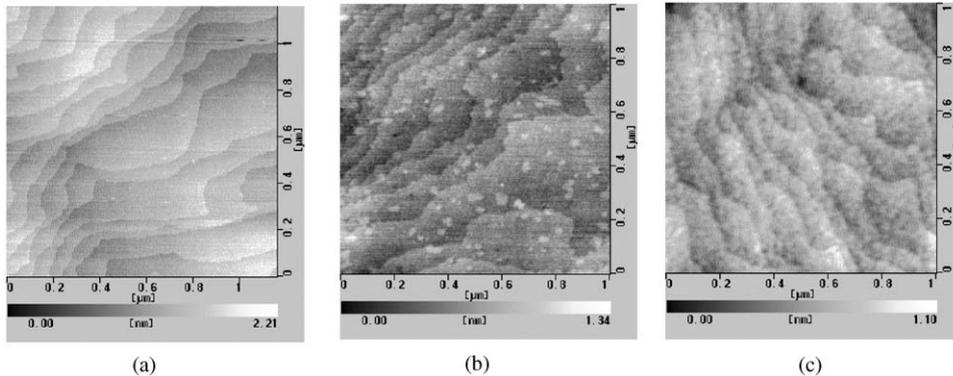


Fig. 3. Tapping mode AFM images for the starting GaAs surface (a) and after atomic hydrogen cleaning with (b) and without (c) arsenic conditions.

features was observed except atomic step. In Fig. 3(b), the two-dimensional small structures have 1 ML thickness, which may be come from As adsorption process under arsenic-rich condition (1.2×10^{-5} Torr). From these results, to achieve highly flat surfaces (like starting surface, as shown in Fig. 3(a)), we adopted low-temperature atomic hydrogen cleaning without arsenic for the formation of nano-hole and trench structures.

Fig. 4 shows selective AFM images for the various oxide structures ($3.8 \times 3.8 \mu\text{m}^2$) patterned by AFM tip-induced oxidation (a) and the nano-hole and trench structures ($3.2 \times 3.2 \mu\text{m}^2$) with depth profile after etched by atomic hydrogen (b). Atomically flat surface and structures free terraces with atomic steps are clearly seen. The oxide structures of surface were etched at optimized conditions ($T_s = 450^\circ\text{C}$, $t_c = 30$ min, H_2 background = 1.0×10^{-6} Torr, and $T_{cc} = 1400^\circ\text{C}$). Before increasing substrate temperature, the atomic hydrogen was irradiated on the GaAs surface. The halo pattern was observed due to amorphous oxide layer while substrate temperature was raised to 450°C . After atomic hydrogen cleaning without arsenic for 10 min, (2×4) reconstruction RHEED patterns appeared. In order to remove the thick oxide structures perfectly, we performed atomic hydrogen cleaning for more 20 min. The highly aligned hole and trench structures with atomically flat surface can be clearly observed. Inset of Fig. 4(b) shows $500 \times 500 \text{ nm}^2$ AFM image of

nano-holes and depth profile. The smallest hole diameter and depth obtained in these experiments are 13.4 and 0.34 nm, respectively. Figs. 4(c) and (d) show a summary on the size distribution of oxide (c) and hole (d) structures, respectively. The aspect ratios of oxide (height/diameter) and hole (depth/diameter) structures are 0.043 and 0.057, respectively. They are slightly different, but it shows that the nano-hole and trench structures reflected their initial oxide structures without atomically flat surface degradation. Therefore, we believe that these hole and trench structures will be also applied to highly aligned quantum dots and wire deposition for quantum dot devices and future applications.

4. Conclusions

Highly aligned nano-hole and trench structures were fabricated by using atomic force microscope (AFM) tip-induced oxidation based atomic hydrogen induced etching on GaAs (001) surface. The nano-hole and trench structures reflected their initial oxide structures without atomically flat surface degradation. The smallest hole diameter and depth obtained in this experiments are 13.4 and 0.34 nm, respectively. From these results, we believe that these nano-structures with atomically flat surface can be important for the realization of the site-controlled nano-structures.

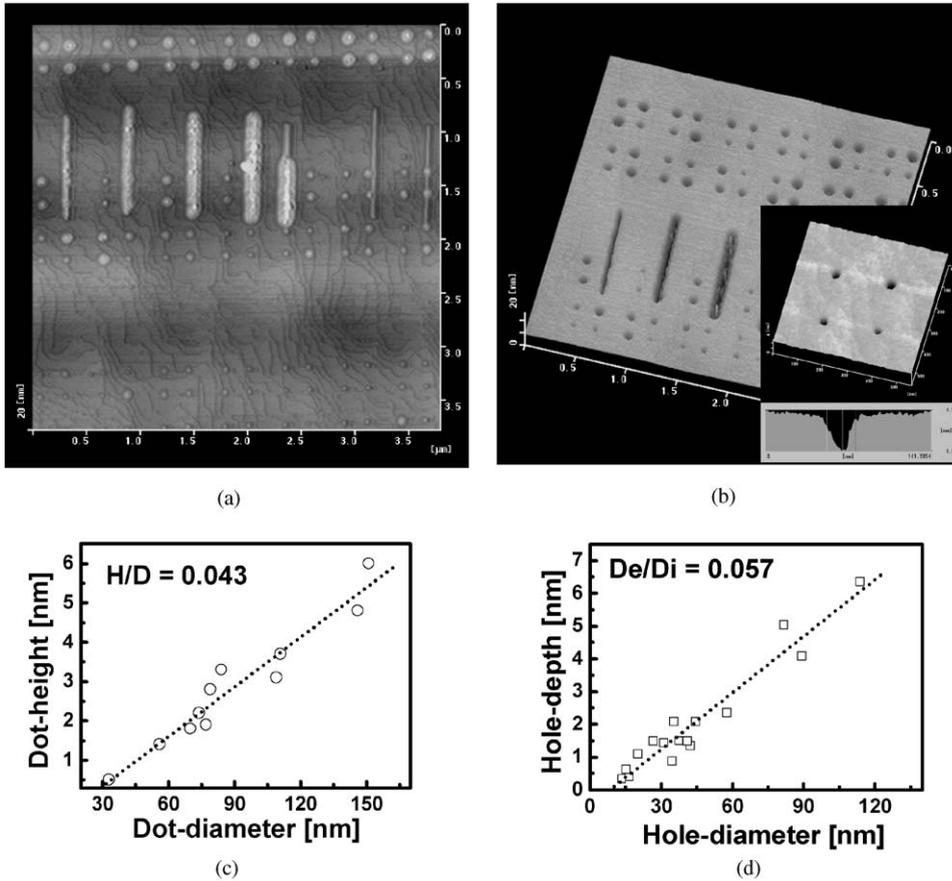


Fig. 4. Tapping mode AFM images for various oxide (a) and nano-hole/trench (b) structures. Summary on the size distribution of oxide dot (c) and nano-hole (d) structures.

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