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EB Patterning Mechanism of GaAs Oxide Mask Layers Used in In-Situ EB Lithography

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In order to clarify the electron-beam(EB) patterning mechanism of GaAs photo-oxide mask layers used in *in-situ* EB lithography, the effects of the surface stoichiometry and heat-treatment of the GaAs photo-oxide mask layers on the patterning characteristics were studied. The threshold dose for EB patterning was shown to depend on the concentrations of oxygen bonded to arsenic(As-O) in the photo-oxide mask layers. For photo-oxide mask layers having higher As-O concentrations, the threshold dose for EB patterning increased, indicating that arsenic oxides mainly worked as a EB/Cl_2 patterning mask. In order to also confirm the role of arsenic oxides, arsenic was desorbed from the photo-oxide mask layers by heat treatment. For photo-oxide mask layers heated at temperatures above 400°C, where stable gallium oxides were thought to be dominant, the mask durability was strengthened and EB/Cl_2 patterning did not occur. These results strongly indicate that arsenic oxides play an important role in EB/Cl_2 patterning in *in-situ* EB lithography.

Introduction

In-situ electron beam (EB) lithography using an ultrahigh-vacuum (UHV) multichamber system is very promising for realizing fine structures on the nanometer-scale.[1] In this technique, an ultra-thin (1-2nm) GaAs photo-oxide layer on GaAs surface is used as a mask for EB patterning and subsequent chlorine (Cl_2) gas etching. Although we previously demonstrated fine-pattern formation and buried quantum-well structures using this technique,[2] the mechanism of EB/Cl_2 patterning has not yet been clarified. To understand the EB patterning mechanism, in this work we studied the effects of the surface stoichiometry and heat-treatment on the EB patterning characteristics of the GaAs photo-oxide mask layers.
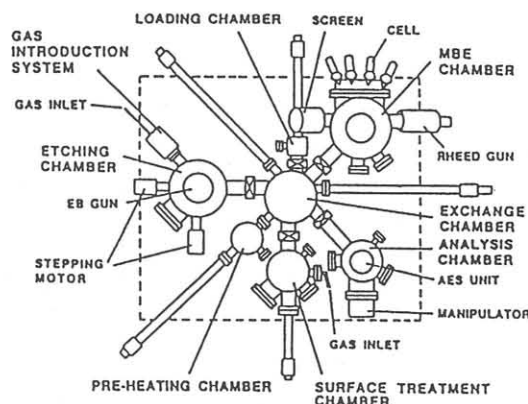
Experimental

Figure 1 shows an illustration of the UHV multichamber system used for *in-situ* EB patterning, which comprises seven chambers for sample loading, sample exchange, preheating, molecular beam epitaxy(MBE), surface treatments (photo-oxidation), Auger electron spectroscopy(AES) analysis, and EB patterning/Cl_2 etching. The experimental procedure to study the effects of the surface stoichiometry on the EB/Cl_2 patterning characteristics comprised the following steps (Fig.2). First, GaAs surfaces (for a 5nm-thick cap layer) with various arsenic (As) coverages were prepared by MBE. The sample structure below this cap layer was a 15 nm thick-GaAs quantum well embedded in AlGaAs barriers (30nm). The reflection high-energy electron diffraction (RHEED) patterns of these surfaces used in this experiment were halo, c(4x4), 2x4 and blurred-2x4 (Blurred) which were obtained by

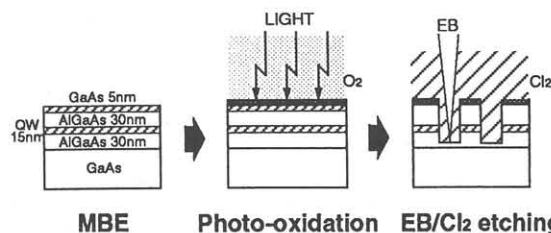Fig.1. Schematic illustration of the UHV multichamber system used in this study.

Fig.2. Process sequence of *in-situ* patterning of GaAs in this study.

the thermal desorption of As in a UHV environment at 100, 300, 480, and 510°C, respectively. The second step was the formation of photo-oxide mask layers on these surfaces in an oxygen gas ambient (1atm, 1h, R.T.) under the illumination of a halogen lamp (138mW/cm^2). The third step was EB writing followed by Cl_2 gas etching in the etching chamber. The electron

beam with an energy of 25 keV was raster-scanned over a rectangular area for EB writing. The beam current was 4.0 nA. The electron dose was varied from 2×10^{17} to 4×10^{19} electrons/cm^2 by changing the EB irradiation time. After EB writing, Cl$_2$ gas etching was carried out for 2 hours at 70°C and a pressure of about 1×10^{-4} Torr. Between these steps, an *in-situ* AES analysis was carried out in the surface analysis chamber.

In order to also study the effect of a heat-treatment on the EB/Cl$_2$ patterning characteristics, GaAs photo-oxide mask layers formed on c(4x4) GaAs surfaces were heat-treated at temperatures between 150 and 450°C for 10 minutes in a UHV environment. Then, EB writing and subsequent Cl$_2$ gas etching were carried out under the same condition as was mentioned above. An *in-situ* AES analysis was also carried out both before and after the heat-treatment.

Results and Discussion

Figure 3 shows the apparent atomic concentrations of As, Ga, and O in photo-oxide mask layers with various As-coverages, which were determined based on the AES derivative peaks of O(510eV), Ga(1070eV), and As(1228eV). The oxygen concentration increased as the surface stoichiometry became arsenic-rich (The concentration of As was increased compared to that of Ga.), indicating that the concentration of oxygen bonded to arsenic (As-O) increased.

Figure 4 shows the EB dose dependence of the etch depth for the above-mentioned GaAs/AlGaAs structures. The threshold dose for EB patterning was shown to depend on the surface stoichiometry. For the 2x4 and blurred surfaces, the threshold doses were about 2×10^{17} electrons/cm^2. For a c(4x4) surface with a higher As-O concentration, it was increased to 7×10^{17} electrons/cm^2. From these results, the threshold dose for EB patterning was proven to become high with increased As-O concentration. For the photo-oxide mask layer on the halo surface(the most As-rich surface), however, the threshold dose decreased to 1×10^{17} electrons/cm^2. In this case, after Cl$_2$ etching, the desorption of a large amount of As from the oxide layer was observed by AES, indicating that a large amount of As, which was thought to be loosely bounded on GaAs, was not completely oxidized, but, rather, prevented the formation of an EB/Cl$_2$ etching mask. (For other photo-oxide surfaces, the desorption of As was not observed after Cl$_2$ etching.)

Concerning the EB irradiation effects on the GaAs photo-oxides, Ide et al recently investigated the adsorption properties of chlorine on EB-irradiated GaAs photo-oxides using X-ray photoelectron spectroscopy (XPS),[3] reporting that the EB irradiation reduced As^{+5} and As^{+3}oxides to As^{2+} and As$^+$ oxides and/or elemental As. They also concluded that these less-oxidized As was preferentially removed by subsequent Cl$_2$ gas exposure compared with the high valency As oxides. This result suggests that the EB/Cl$_2$ patterning of GaAs oxide is caused by such a modification of arsenic oxides by EB irradiation, being consistent with the EB patterning characteristics, depending on the As-O
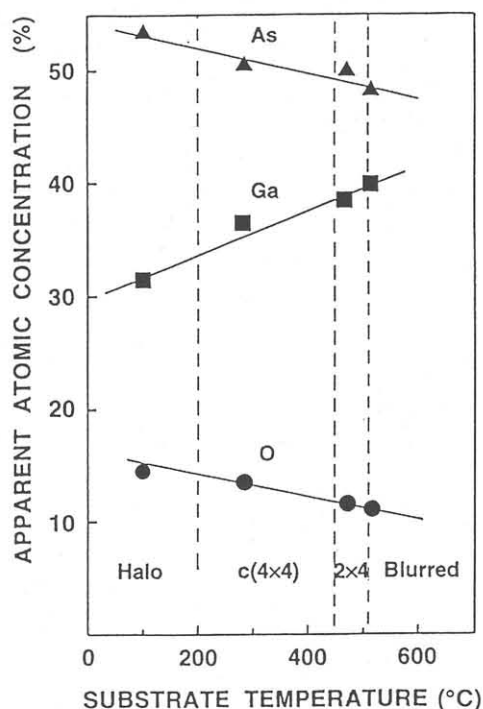

Fig.3. Apparent atomic concentrations of As, Ga, O for GaAs photo-oxide mask layers for various As-coverages, which were determined by the AES derivative peaks of O(510eV), Ga(1070eV), and As(1228eV).
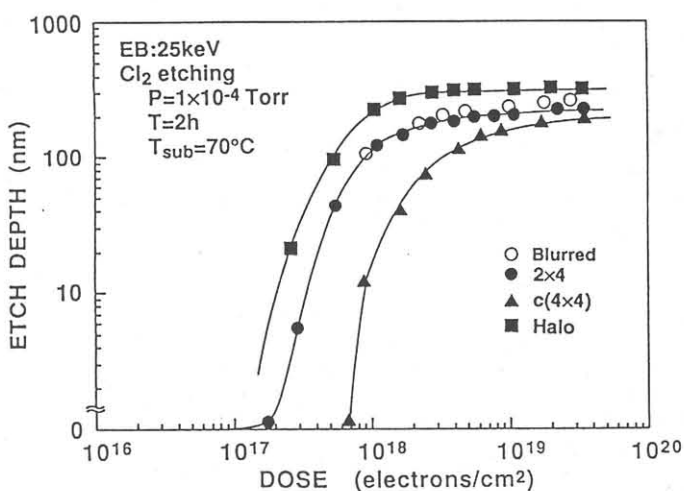

Fig.4. EB dose dependence of the etch depth for GaAs/AlGaAs with GaAs photo-oxide mask layers for various surface stoichiometries.

concentration, as mentioned in Fig.4. Namely, the photo-oxide masks with higher As-O concentration require a greater electron dose for patterning compared with the case of a lower As-O concentration. Thus, the threshold dose became high with increasing As-O concentrations. Considering the above-mentioned results, arsenic oxides were shown to play an important role in EB patterning/Cl$_2$ etching.

Further, in order to clarify the role of arsenic for EB patterning, arsenic was desorbed from the oxide layers(c(4x4) GaAs surface) by a heat treatment. Figure 5 shows the AES peak ratio of As/Ga, O/Ga for photo-oxide mask layers which were heat-treated at 150~450°C in a UHV environment. The AES peak ratio of As/Ga was reduced when the photo-oxide mask layer was heated at temperatures above 300°C, while the peak ratio of O/Ga was almost unchanged in the temperature range used here.

Figure 6 shows the EB dose dependence of the normalized etch depth for these heat-treated photo-oxide masks. At a heat-treatment temperature of 150°C, at which arsenic did not desorb, the patterning characteristics were almost unchanged. However, remarkable changes in the patterning characteristics were observed at temperature above 330°C. For a photo-oxide mask heated at 330°C, where arsenic began to desorb, the threshold characteristics became degraded compared with a non-heated sample, despite an almost unchanged threshold dose. In this case, many etch-pits on the photo-oxide mask were observed after Cl_2 etching, indicating that the mask durability against Cl_2 gas was locally weakened. On the contrary, when the photo-oxide mask was heated at temperature above 400°C, the mask durability became strengthened, and, thus, EB patterning /etching did not occur. This drastic change in the oxide mask characteristics may be due to the formation of stable Ga-oxide, such as Ga_2O_3, caused by arsenic-desorption to a great amount.[2] (Tone et al reported that after As-desorption, oxygen which was originally bonded to As was transferred to Ga, resulting in the formation of stable Ga_2O_3.[4])

From these results, it was shown that the oxygen bonded to gallium was not modified by EB irradiation under the above-mentioned condition. It was therefore proven that gallium oxides did not work as an EB/Cl_2 patterning mask.

Summary

To understand the EB/Cl_2 patterning mechanism in *in-situ* EB lithography, the effects of the surface stiochiometry and heat-treatment on the EB/Cl_2 patterning characteristics were studied. First, arsenic oxides were shown to play an important role in EB/Cl_2 patterning of the photo-oxide mask layer. GaAs photo-oxide mask layers with a higher As-O concentration increased the threshold dose for EB patterning, due to much arsenic oxide. Next, the photo-oxide mask layers where arsenic was desorbed by a heat-treatment, were also shown to change the EB patterning characteristics. For a photo-oxide mask layer heated at 330°C, the EB patterning characteristics and mask durability against Cl_2 gas became degraded. At temperature above 400°C, the photo-oxide mask, which was thought to consist of stable gallium oxides, was not modified by EB irradiation. From these results, it was revealed that the EB/Cl_2 patterning of GaAs photo-oxide used in *in-situ* EB lithography is caused by a modification of the arsenic oxides by EB irradiation.

Therefore, the control of the As-O concentrations in a GaAs photo-oxide mask layer is essential for fine EB patterning in *in-situ* EB lithography.
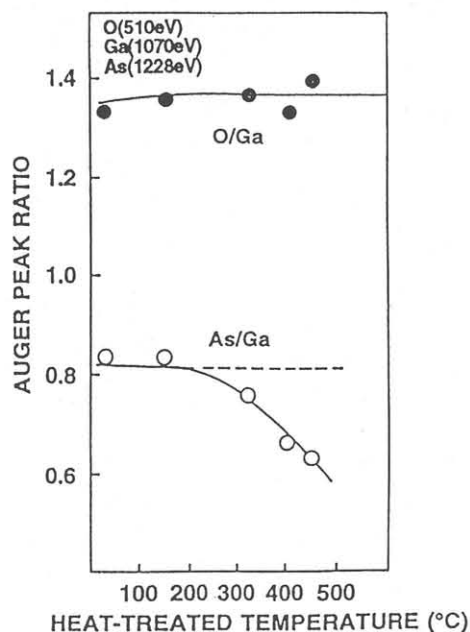
Fig.5. AES peak ratio of As/Ga, O/Ga for GaAs photo-oxide mask layers as a function of the heat-treatment temperature.
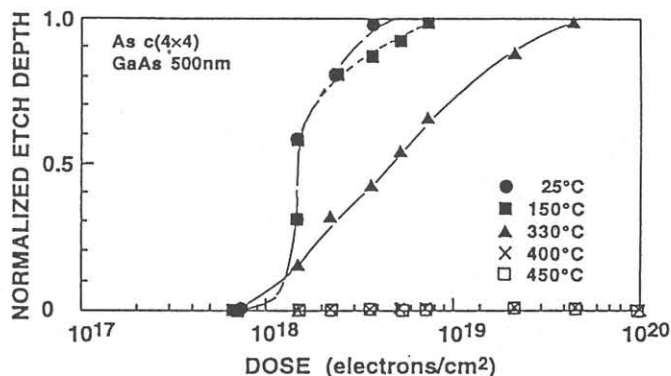

Fig.6. EB dose dependence of the normalized etch depth for GaAs/AlGaAs with heat-treated photo-oxide mask layers.

References

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