New processing techniques for optoelectronic devices with low-dimensinal quantum structures

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A new semiconductor processing technology for optoelectronic devices with low-dimensional quantum-structures, developed at Optoelectronics Technology Research Laboratory (OTL), is reviewed. This technology for a GaAs-AlGaAs material system includes epitaxy controlled on the atomic scale and *in situ* pattern-formation as well as their combination. The emphasis of the paper will be put on the *in situ* and real-time characterization of epitaxial growth using μ-RHEED and STM.

1. Introduction

There has been a strong interest to apply 2- and/or 3-dimensional semiconductor nanostructures to optoelectronic devices motivated by the expected improvement of performance.[1] For such purposes, a technology capable of fabricating arbitrarily designed fine structures on the nm scale is essential. A variety of attempts have been made to fabricate such nanostructures.[2,3] Recently, many authors have tried to grow quantum-wires and boxes using epitaxy on pre-patterned substrates with the aid of lithography.[4] That is, nm-scale semiconductor heterostructures are being fabricated by the combined use of epitaxy controlled on the atomic scale and lithography on the nm scale.

However, since such nanostructures are very sensitive to surface and/or interface contamination, the processing technologies used to fabricate them must be chosen while placing emphasis on cleanliness of the obtained interfaces. Therefore, *in situ* processing, in which all of the necessary processes, such as epitaxy and pattern formation, are conducted under an ultra-high vacuum (UHV) condition or in a controlled ambient without being exposed to the air, is regarded as being a most hopeful candidate.[5]

In this direction, we have made a systematic study of epitaxy and patterning techniques compatible with *in situ* processing in order to fabricate semiconductor nanoheterostructures. In this study, information obtained using various surfaceanalytical techniques was quite useful.

2. Epitaxy and *In Situ* Characterization

To control epitaxial growth on the sub-nm scale, it is important to understand the dynamical behavior of the constituent atoms on the growing surface, as well as the surface structure of the substrate on the atomic scale. For such purpose, we have developed several epitaxial systems combined with surfaceanalysis methods.

2.1 Atomic Structure of Epitaxial Surfaces *In situ* Observed by STM

With the advent of scanning tunneling microscopy (STM), it has become possible to observe individual atoms at the surface of semiconductors.[6] We have made an *in situ* scanning tunneling microscope observation of the surfaces of homoepitaxial GaAs/GaAs layers grown by molecular beam epitaxy (MBE), using a multi-chamber UHV-STM system equipped with an MBE facility.[7]

The substrates used for this experiment were GaAs (100) and vicinal surfaces. After thermal cleaning, 30 MLs of GaAs were grown at 590 °C. This is the minimum necessary thickness to obtain a clean surface which can provide atomically resolved STM images. For the STM observation the sample was transferred to the STM chamber. It is considered that the observed structure was nearly the same as the surface structure of the original substrate, since 30 MLs of GaAs would not alter the gross features of the original surface. After the STM observation, the sample was transferred back into the MBE chamber and a ~1.5 μm thick GaAs layer was grown under the step-flow mode. The surface of the epitaxial layer was then observed with the STM using the same procedure as described above.

Figures 1(a) and (b) show STM images of the 30 ML GaAs grown surface and the surface of a 1.5 μm thick grown GaAs layer. The dark lines running in the [1$\bar{1}$0] direction reflectmissing As dimer rows. In the image, wide flat

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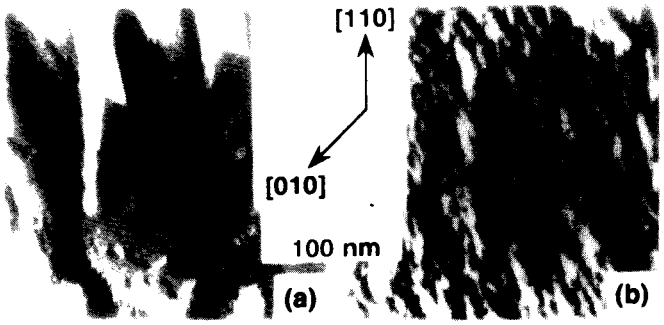


Fig. 1 STM images of (a) a 30 ML GaAs grown surface, representing the atomic structure of the substrate surface and (b) a 1.5 μm GaAs grown surface. The scanning area is 280 x280 nm^2.

terraces, narrow terraces, small vacancies and several deep holes of ca. 50~100 nm can be seen. It should be noted that the narrow terraces are nearly parallel to the [110] direction and the wide terraces are perpen-dicular to this direction. The misorientation by 2 degrees is considered to be shared by these terraces. These are 'real' features of the substrates used for MBE growth, and demonstrate the importance of proper choice of substrate for 'atomically flat' epitaxy.

In figure 1(b), the step-down direction is from the upper-right to the lower-left. In this image, it can be seen that the rugged terraces along the [010] direction are scattered in a relatively uniform way. That is, (i) the rather straight edges which run parallel to the fine dark lines in the [1$\bar{1}$0] direction show the missing dimer rows (A-type step); (ii) the rugged edges running parallel to the [110] direction (B-type steps) and edges running in the [100] direction (mixture of A- and B-types) can also be seen.

From a detailed study of a similar STM observation, it turned out[8] that the step-structures change depending on the different misorientation degrees and the growth conditions. For example, by optimizing the vicinal angle and the growth conditions, both the A- and B-steps became rather straight.[9]

2.2 Dynamical Behavior of the Growing SurfaceObserved by Real-Time μ-RHEED

We have carried out a microscopic and dynamical study of the growing surface using Micro-Probe Reflection High-Energy Electron Diffraction (μ-RHEED).[10] For this purpose, a combined system of μ-RHEED/MOMBE, the schematic structure of which is shown in Fig. 2, was developed.[11]

Figure 3 shows μ-RHEED images of an MBE-growing GaAs (100) surface and its schematic structure.[11] Sub-micron order textured structures extending along the [1$\bar{1}$0] direction can be seen. The details concerning the tex-tured

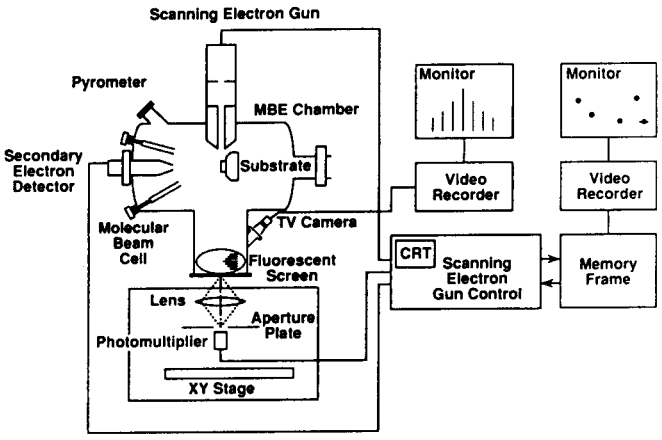


Fig. 2 Schematic diagram of μ-RHEED/ MBE system.

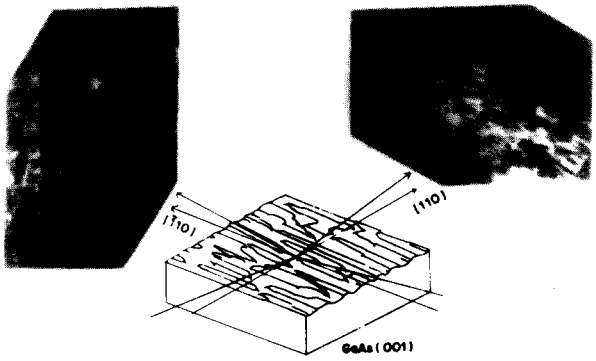
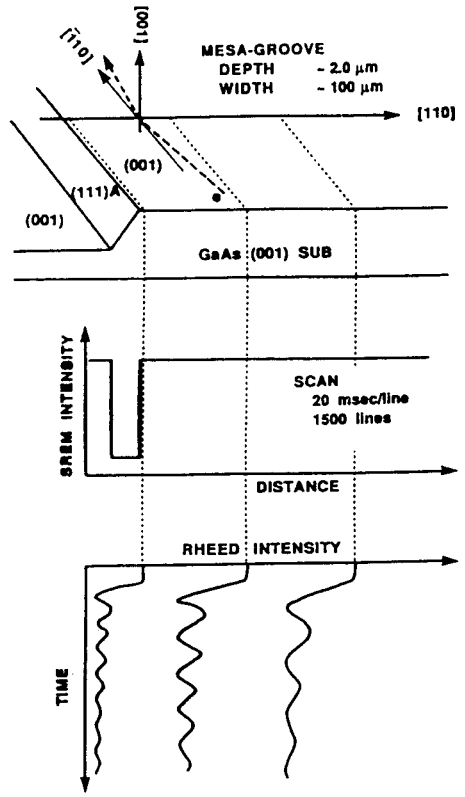


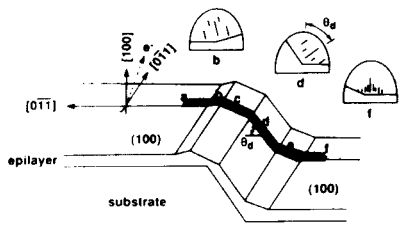
Fig. 3 μ-RHEED images of MBE-grown GaAs (001) using the specular beam spots of incident azimuth along [110] and [1$\bar{1}$0] together with a conceptualization of the surface undulation feature.

structures which develop as epitaxial growth proceed were observed. That is, that the GaAs (100) surface was rather unstable at the MBE growth temperatures. These features have recently been confirmed by an AFM obser-vation.[12] This is a phenomenon which is rather unfavor-able to nanofabrication.

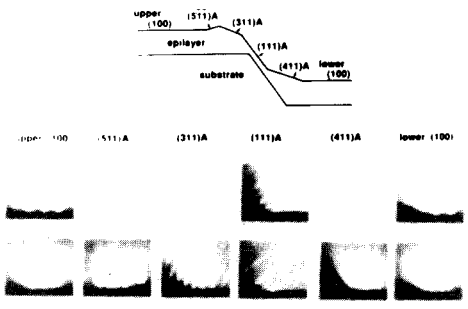
A novel method to determine the migration length of Ga atoms during MBE-growth was developed using μ-RHEED.[13] For example, on a substrate as shown in Fig. 4(a), the MBE-growth rate of GaAs on the (001) surface is enhanced by the migration of Ga atoms which fall on the (111)A facet.[14] The microscopic growth rate of the GaAs on mesa-etched GaAs (001) during growth was measured as a function of the distance from the edge using μ-RHEED.

From a simple analysis of this measurement, the migration length of Ga atoms during MBE was determined.[13] The values obtained by this method are ~1 μm along the [110] direction and several μm along the [1$\bar{1}$0] direction (Fig. 4(b)), which are about 2 orders of





(a)



(b)

Fig. 4(a) Schematic illustration of the method to observe microscopic distribution of growth rate using μ-RHEED. (b) Surface migration length of Ga atoms during MBE-growth along [110] and [$\bar{1}$10] directions on GaAs (100) surface.

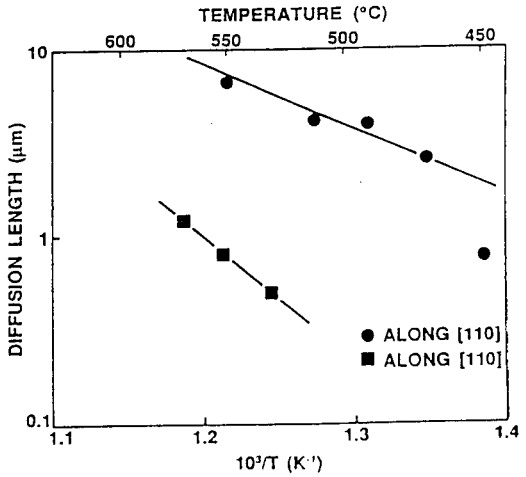


Fig. 5 (a) Schematic illustration of method to observe facets evolution on micro-patterned substrates and (b) the μ-RHEED diffraction patterns from the facets before growth (upper patterns) and from the facets after growth (lower patterns).

magnitude larger compared with the values derived conventionally from the extinction of RHEED oscillation.[15] The observed large values for the migration length give more hopeful data about the self-organized epitaxy for the fabrication of nanostructures.

The μ-RHEED method is also useful for observing facet evolution during epitaxial growth on patterned substrates, as demonstrated in Fig. 5.[16]

3. *In-situ* Patterning for Nanofabrication
- *In-situ* Electron-Beam (EB) Lithography -[17]

In this method, which we call *in situ* electron-beam (EB) lithography, an ultra-thin surface oxidized layer of GaAs is used as both an electron-sensitive resist film and an etching mask, and can be removed by heating. The basic processes of *in situ* EB lithography are either a local modification of the surface oxide layer of GaAs by the irradiation of an electron beam and subsequent etching off of the modified portions by Cl_2 gas ('positive'-type lithography),[18] or electron beam-induced local oxidation of GaAs and a following pattern transfer by Cl_2 gas etching ('negative'-type).[19] In Fig. 6, the process sequences of *in situ* EB lithographies are illustrated for both the 'positive' and 'negative' types.

The 'positive'-type *in situ* EB lithography process comprises the following six steps:[18] 1) preparation of a clean GaAs surface by molecular beam epitaxy (MBE) on an appropriate GaAs substrate. 2) formation of an ultra-thin surface oxide layer in a clean oxygen ambient under the illumination of light, 3) modification of the oxide layer by

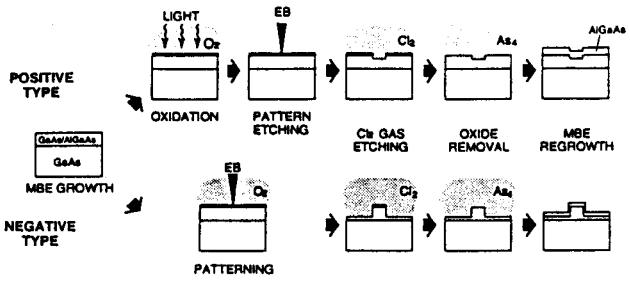


Fig. 6 Schematic illustration of the process sequences of the *in situ* EB-lithographies for 'positive' and 'negative' types.

the irradiation of electron-beam and subsequent removal of the oxide layer by Cl_2 gas at the an area modified by the electron-beam as pattern drawing, 4) Cl_2 gas etching of underlying layer as pattern transfer, 5) removal of oxide layer by heating under an As_4 ambient, and 6) MBE regrowth. All of these processes can be repeated without exposing sample surface to air, which results in the fabrication of 3-dimensionally designed nanoheterostructures.

In a variation of *in situ* EB-lithography,[19] negative'-type, direct patterning is made on a clean surface of GaAs by electron-beam irradiation under a pure oxygen atmosphere and subsequent Cl_2-etching, as illustrated in the lower column of Fig. 6. The electron-beam irradiation enhances the oxidation; this electron-beam stimulated oxide is also resistive to the chlorine gas etching and can act as an etching mask. In this process, the parts where the electron beam is irradiated are left unetched. So, we may call this process as 'negative'-type lithography in analogy with conventional lithography.

The minimum features fabricated are about 20 nm, which is close to the minimum radius of electron-beam at 25 keV of our experimental system. Considering that the thickness of the GaAs oxide mask is about 1 nm, we may say that the spatial resolution is limited mainly by the radius of electron beam. The spatial resolution will be improved by improving electron-beam system, for example, by increasing the acceleration energy.

Surface-scientific aspects: The mechanisms for the electron beam-induced patterning was studied by various surface analytical methods, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and temperature programmed desorption (TPD). Ide and Yamada found using an XPS that the chlorine gas adsorbs on the electron-beam irradiated photo-oxides of GaAs while only a very small amount of adsorption of chlorine atoms is seen on the as-formed GaAs photo-oxides.[19] The electron dose necessary for adsorption of chlorine gas was on the same order as the EB-dose for patterning. They found, further, that the irradiation of an electron beam causes a change in the oxidized states of As, and considered that the chlorine exposure triggers the preferential removal of EB-induced As suboxides (or elemental As) in the forms of $AsCl_x$ and that this is the key to patterning a photo-oxide mask.

Merit of in situ Processing: A control experiment was performed in order to clarify why *in situ* processing is necessary.[21] Three kinds of samples with the same structure were fabricated. (i) samples subjected to *in situ* chlorine etching and regrowth, (ii) reference samples grown by continuous MBE and (iii) samples once exposed to air and taken into the MBE-chamber. Comparison of photo-luminescence (PL) spectra for the process-induced damage of *in situ* and *ex situ* fabricated specimens showed the superiority of the all UHV-processing or *in situ* processing.

4. A Future Direction - Integration of Self-Organized Epitaxy and *In situ* Lithography

As described above, the combination of atomically controlled epitaxy and *in situ* nano-lithography is one way to fabricate 3-dimensional superstructures. Beside this, the utilization of epitaxy on a prepattern substrate[4] or on a surface of a lattice-mismatched material system[23] has recently been receiving a strong attention, since this method can be used to fabricate the quantum-wire and-or -box structures by epitaxy only; therefore, the obtained nanostructures are expected to have good quality.

However, it is almost impossible to fabricate arbitrarily designed structures, which is being requested in order to optimize device performance or the new physics contained therein, by epitaxy alone. *In situ* EB-lithography also has a practical limit of around 10 nm. Thus, the incorporation of self-organized epitaxy into *in situ* EB-lithography as an elemental process will be one possible solution to these two methods. Actually, this kind of approach is rapidly increasing.

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