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New approach to local anodic oxidation of semiconductor heterostructures

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ABSTRACT

We have experimentally explored a new approach to local anodic oxidation (LAO) of a semiconductor heterostructures by means of atomic force microscopy (AFM). We have applied LAO to an InGaP/AlGaAs/GaAs heterostructure. Although LAO is usually applied to oxidize GaAs/AlGaAs/GaAs-based heterostructures, the use of the InGaP/AlGaAs/GaAs system is more advantageous. The difference lies in the use of different cap layer materials: Unlike GaAs, InGaP acts like a barrier material with respect to the underlying AlGaAs layer and has almost one order of magnitude lower density of surface states than GaAs. Consequently, the InGaP/AlGaAs/GaAs heterostructure had the remote Si–δ doping layer only 6.5 nm beneath the surface and the two-dimensional electron gas (2DEG) was confined only 23.5 nm beneath the surface. Moreover, InGaP unaffected by LAO is a very durable material in various etchants and allows us to repeatedly remove thin portions of the underlying AlGaAs layer via wet etching. This approach influences LAO technology fundamentally: LAO was used only to oxidize InGaP cap layer to define very narrow (~50 nm) patterns. Subsequent wet etching was used to form very narrow and high-energy barriers in the 2DEG patterns. This new approach is promising for the development of future nano-devices operated both at low and high temperatures.

1. Introduction

The semiconductor industry has made substantial progress in the last decade: the elementary building blocks of electronic structures have been downscaled from the sub-micron to nanometre scales. A further reduction of their size down to 40 nm and beyond is complicated because of fundamental physical limits. Consequently, new approaches, involving materials and technologies, must be taken to be able to manufacture such small devices and make them beneficial.

In materials research, one possible way to tackle the challenge is to replace the base structure: Instead of bulk silicon, a semiconductor heterostructure with a two-dimensional electron gas (2DEG) can be used. A promising candidate for this purpose is an AlGaAs/GaAs-based heterostructure, which is the most common and well researched from a large variety of semiconductor heterostructures. The 2DEG is confined at the interface between AlGaAs and the GaAs buffer layer of the heterostructure. It is supplied with electrons from the remote Si–δ doping layer.

The fact to be noted is that the surface of the AlGaAs layer must be protected, usually with a layer of GaAs, because it suffers from a high reactivity of Al to oxygen and from high densities of deep levels.

However, using GaAs as the cap layer material has two disadvantages: (1) like AlGaAs it has also a high density of surface states, and (2) it is the well material in the AlGaAs/GaAs system. This necessitates that the heterostructure must be carefully designed to make sure that charge carriers fill the 2DEG and not the GaAs surface states. To ensure it, Graf et al. placed the remote Si–δ doping layer 17 nm beneath the top surface. Fig. 1a exemplifies their heterostructure with the 2DEG layer placed 34 nm beneath the surface [1]. It is relatively deep for the formation of patterns with a lateral resolution smaller than 40 nm.

To avoid the drawbacks, we have designed, grown and tested an AlGaAs/GaAs-based heterostructure capped with an InGaP layer. The heterostructure was grown by organo-metallic vapour phase epitaxy (OMVPE). Using InGaP as the cap layer is favourable because (1) InGaP is a barrier material in the AlGaAs/GaAs system and (2) it has a density of surface states one order of magnitude lower compared with that of GaAs. Thus in an InGaP/AlGaAs/GaAs heterostructure, the remote Si–δ doping layer can be placed only 6.5 nm beneath its surface. The 2DEG layer is then formed 23.5 nm beneath the surface (Fig. 1b). Such a shallow 2DEG is suitable for the formation of patterns laterally downscaled to 40 nm and beyond.

To manufacture nano-metre-sized structures and devices that can be operated both at low and high temperatures, the technology and processing must ensure that lithographic patterns are accurately transferred into the 2DEG layer with a resolution on the nano-metre scale. Also, the patterns must possess sufficient lateral insulating properties.

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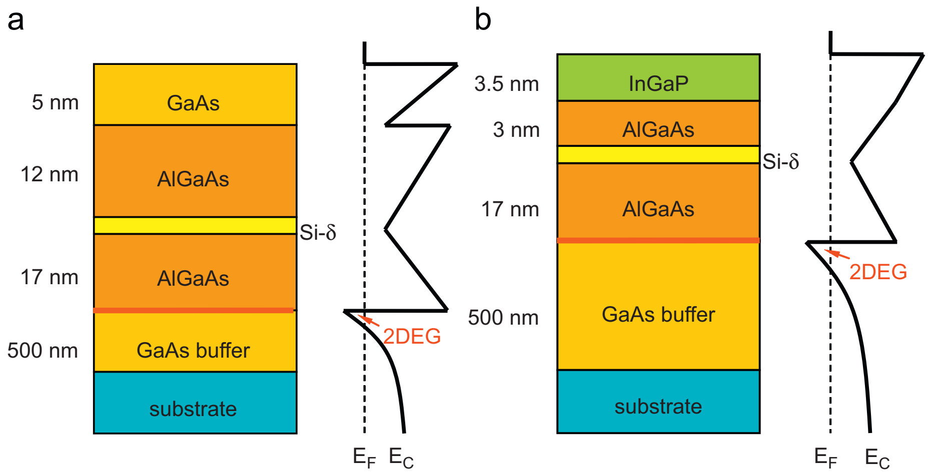

Fig. 1. (a) Standard AlGaAs/GaAs heterostructure with a GaAs cap layer and a 2DEG placed 34 nm beneath the surface; (b) our heterostructure grown by OMVPE with an InGaP cap layer and a 2DEG placed 23.5 nm beneath the surface.

From among nano-metre patterning techniques, local anodic oxidation (LAO), realized by the tip of an atomic force microscope (AFM) [2], represents the simplest way to reproducibly manufacture nano-scale patterns. The principle of LAO lies in the oxidation of a sample by a negative voltage applied to the AFM tip with respect to the sample. If the local electric field reaches 10^9 V/m [3], molecules from the water bridge located between the tip and the sample [4] are disintegrated into H^+ and OH^- ions. The OH^- ions are transported and accelerated by the local electric field towards the sample, where they form oxides. As the AFM tip is scanned over a sample surface during the oxidation process, a desired pattern is created in the form of oxide lines.

If one applies LAO to a semiconductor heterostructure with a 2DEG [5] confined near beneath the surface (less than 40 nm), the 2DEG layer is completely depleted right under the area affected by LAO [6]. Well-depleted areas represent high potential barriers (reliable lateral insulation) for the 2DEG outside the oxidized area. In this way, one can shape a 2DEG layer to prepare various quantum structures and devices [7–9].

Heterostructures with a shallow 2DEG layer are always capped with a low-conducting layer of GaAs. However, this entails that the maximum electrical field at the very beginning of a LAO process is shifted away from the end of the AFM tip towards outer parts of the water bridge [10–11] (Fig. 2). As a consequence, oxide lines formed under the tip are formed relatively wide even if a sharp tip is used.

To sufficiently deplete the 2DEG layer of a standard heterostructure [1], it is necessary to deeply oxidize the sample to affect the remote Si–δ doping layer. However, oxide lines as high as 15 nm have their base as wide as ~130 nm, which considerably worsens the lateral resolution of LAO. Hence, it seems to be impossible to reach a desired lateral dimension down to 40 nm and less in this way.

To overcome this limitation, we used a new approach in LAO technology using the heterostructure with the InGaP cap layer. We only oxidized the InGaP cap layer and formed 3 nm high oxide lines. Such lines could be as thin as 40 nm or even less. The lines were not used to deplete the 2DEG. They served to define the patterns in the InGaP layer. The patterns were subsequently etched away to expose the underlying AlGaAs to be oxidized. Native oxides the AlGaAs layer were subsequently etched away via lines opened in the InGaP layer. The process of formation and removal of oxides from the AlGaAs was repeated several times to transfer the patterns into the 2DEG layer.

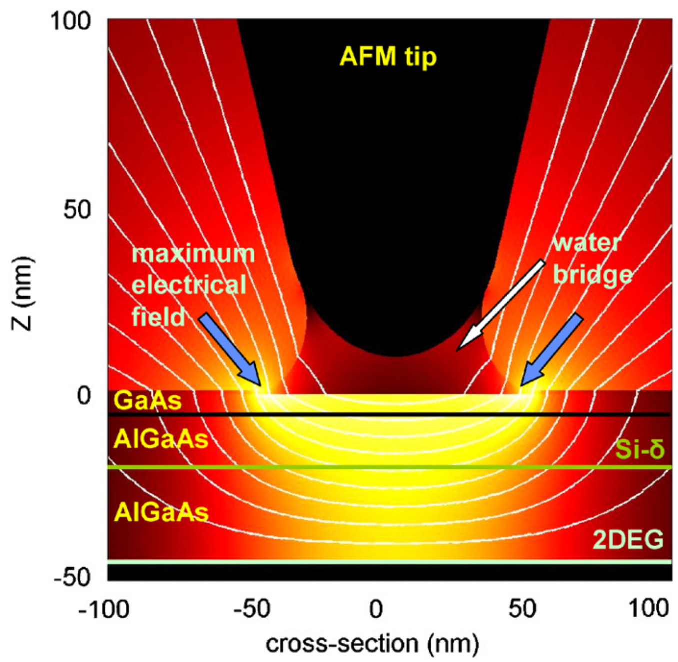

Fig. 2. Maximum electrical field at the very beginning of the LAO process is shifted away from the end of the AFM tip towards outer parts of the water bridge. As a consequence, the lines formed by the tip will be wide even if a sharp tip is used.

This paper reports on a new approach to using LAO for the formation of nano-scale structures. As shown below, the new approach makes it feasible (1) to define patterns by LAO and the subsequent wet etching of a heterostructure capped by InGaP, and (2) to prepare potential barriers on the heterostructure under study.

2. Experiment

2.1. Design, growth and testing of a heterostructure

To design an appropriate heterostructure for the LAO experiment, we tested several heterostructures prepared by low-pressure OMVPE on vicinal (1 0 0) semi-insulating GaAs substrates using Aixtron AIX 200 equipment.

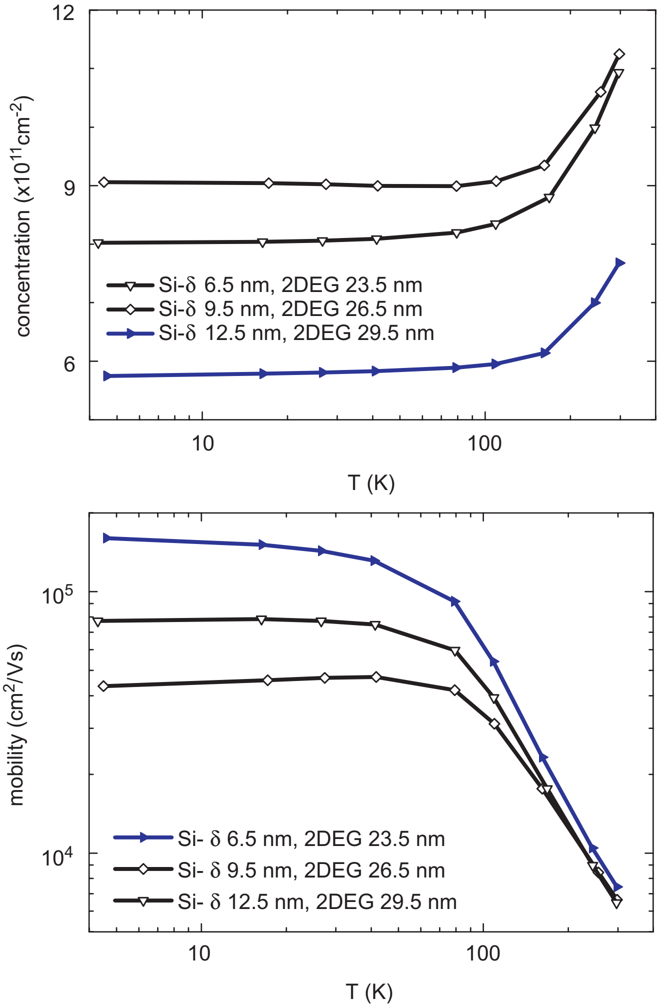

Fig. 3. Concentration and mobility of charge carriers of the 2DEG versus temperature for the heterostructure used for the LAO experiment and for other heterostructures with the remote Si–δ doping layers at a depth of 9 and 12 nm.

One heterostructure was selected for the LAO experiment. It consisted of a 500 nm GaAs buffer layer, a 17 nm AlGaAs spacer, a remote Si–δ doping ($N_D = 8.6 \times 10^{12}\,cm^{-2}$), a 3 nm AlGaAs cover layer, and a 3.5 nm strained $In_{0.36}Ga_{0.64}P$ cap layer. The remote Si–δ doping and 2DEG were placed 6.5 and 23.5 nm beneath the surface, respectively.

Fig. 3 shows the concentration and mobility of charge carriers of the 2DEG versus temperature. It also shows the dependencies for heterostructures that had the remote Si–δ doping layers at a depth of 9 and 12 nm.

Hall bars with 5 μm wide arms were defined on the heterostructure by optical lithography. Milling with neutralized argon ions was used for the mesa definition. The Hall bars were provided with InSn ohmic contacts to access the 2DEG. Samples with the Hall bars were mounted onto chip holders and wired.

2.2. LAO experiment

The experiment was carried out using an NT-MDT NTegra AFM in an airtight chamber under a controlled ambient humidity of 50%. The AFM was operated in non-contact mode with a closed feedback loop at a cantilever resonant frequency of 365 kHz, a typical force constant of 14 N/m, and a set point of 9%. Oxide lines were formed under a commercial n-doped silicon tip with a resistivity of 0.01–0.05 Ω cm. The tip curvature radius was less than 10 nm and the full tip cone angle was less than 10° along 200 nm away from the tip apex.

The tip was biased with respect to the sample by a square wave AC voltage at a frequency of 280 Hz, a 50% duty cycle, and peak-to-peak amplitude of 23 V. A reset voltage of 4 V was used [12]. The tip speed was 0.5 μm/s during oxidation.

Under the above conditions, we formed an oxide line across one arm of a Hall bar. The height and the base width of the line were $h = 2.4 \pm 0.3$ nm and $w_o = 74.3 \pm 3.3$ nm, respectively. The oxides were removed from the line in a NH_4OH solution during 20 s. This left a trench in the sample. Its depth and the pithead width were $d_1 = 3.4 \pm 1.1$ nm and $w_1 = 52.0 \pm 8.2$ nm, respectively. The sample was then exposed to ambient air during 24 h, after which the native oxides were removed by the same etching process. The depth and the pithead width of the re-oxidized and re-etched trench were $d_2 = 17.1 \pm 0.9$ nm and $w_2 = 95.9 \pm 8.4$ nm, respectively. Fig. 4 shows the surface topographies and cross sections after the LAO, the 1st and the 2nd runs of wet etching.

All scans were performed in non-contact mode with a fresh AFM tip on a softer cantilever with a resonant frequency of 136 kHz and a typical force constant of 4.5 N/m. A set point of 38% was applied. The other parameters were the same as those used for the LAO. The scans were preformed in the airtight chamber in which the samples were dried by nitrogen gas.

I–V characteristics at 77 K (Fig. 5) were measured on the two-terminal device (inset of Fig. 5) to evaluate the individual processing stages after LAO, after the 1st etch run, after the 24 h long exposure in ambient air, and finally after the 2nd etch run.

3. Results and discussion

LAO is commonly used to form nano-scale patterns in a shallow 2DEG of an AlGaAs/GaAs-based heterostructure directly via a depletion of the 2DEG. Unlike this mainstream approach, our technique uses LAO only to form nano-scale patterns in an InGaP cap layer of an AlGaAs/GaAs-based heterostructure. The patterns are subsequently transferred further to deplete the 2DEG by a series of small precise steps of formation of native oxides and their wet-etch removal.

In the first step, we formed linear oxide patterns in the 3.5 nm thick InGaP cap layer. As the layer was thin, the patterns were only ~3 nm high. We believe that such lines can be made as thin as 40 nm or even less. The *I–V* characteristics measured after the LAO showed that the 2DEG was not depleted (full squares). The oxides created by LAO probably did not affect the remote Si–δ doping layer.

The oxides were removed from the linear patterns by wet chemical in the second step. This led to linear patterns in the form of trenches whose depth was such that the underlying AlGaAs layer was just exposed to the ambient air. When AlGaAs is exposed to air, it oxidizes and shows a density of surface states that is almost one order of magnitude higher than that of InGaP. As a result, electrons from the 2DEG were preferentially captured by the surface states along the trench lines. The *I–V* characteristics after the 1st etch run (open circles) showed that the potential barrier formed in this way exhibited a breakdown voltage of 380 mV (at the current of 200 pA).

To increase the number of captured charge carriers, i.e. to increase the potential barrier height, the sample was exposed to ambient air during 24 h for further native oxide growth. The *I–V* characteristics measured after this step (full triangles) showed the breakdown voltage of the potential barrier reached 750 mV. The native oxides probably cut through the remote Si–δ doping closer to the 2DEG layer.

The native oxides, formed in the second step, were removed by the same etching process in the third step. The *I–V* characteristics measured after the third step (open triangles) showed that no current flowed between the terminals. The remote Si–δ doping

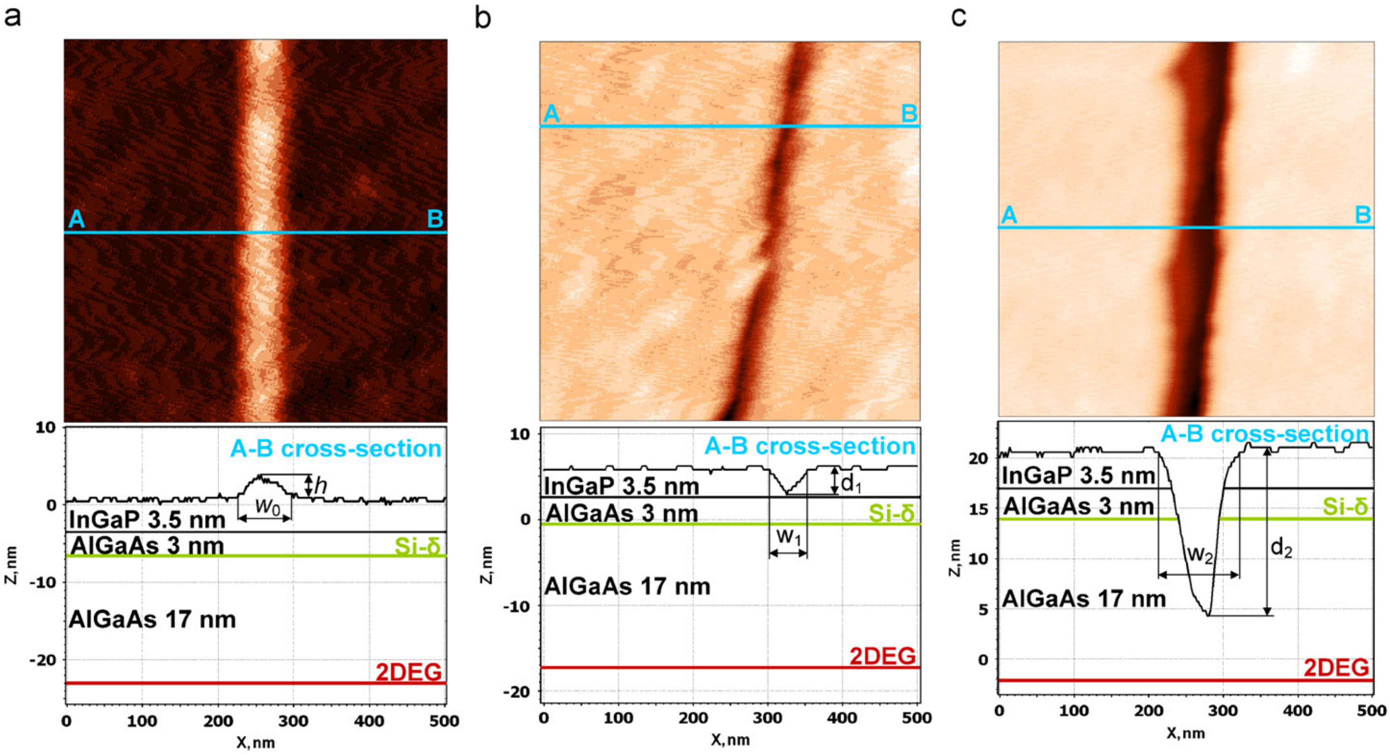

Fig. 4. (a) Oxide line after the LAO, $h = 2.4 \pm 0.3$ nm, $w_o = 74.3 \pm 3.3$ nm; (b) trench after the 1st etch run, $d_1 = 3.4 \pm 1.1$ nm, $w_1 = 52.0 \pm 8.2$ nm; and (c) trench after the 2nd etch run, $d_2 = 17.1 \pm 0.9$ nm, $w_2 = 95.9 \pm 8.4$ nm.

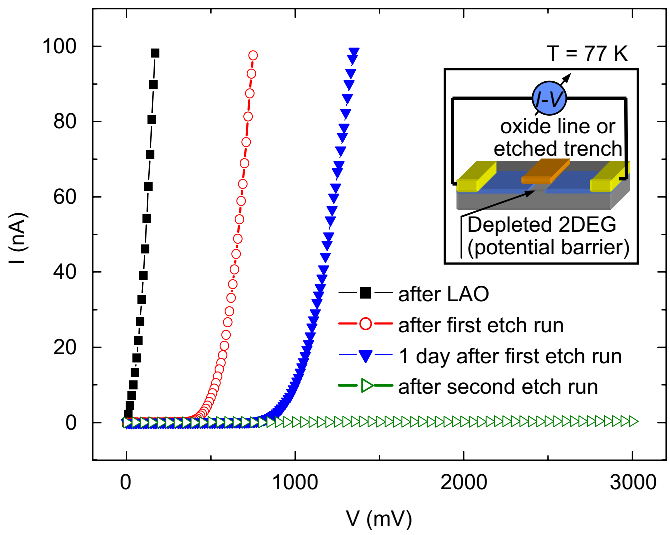

Fig. 5. I–V characteristics at 77 K measured on a two-terminal device (inset) after LAO, after the 1st etch run, after exposure for 24 h in ambient air, and finally after the 2nd etch run.

layer and the 2DEG layer were probably cut through fully by native oxides formed in the trenches, which led to the formation of completely isolated regions in the 2DEG layer.

4. Conclusion

We report on a new approach to using LAO for the definition of linear potential barriers on an InGaP/AlGaAs/GaAs heterostructure with a 2DEG. LAO and subsequent sequential wet etching were used to form linear trenches as thin as ~50 nm on the heterostructure. Although the trenches are relatively thin, we believe that they can be made even thinner using the approach. The topographic homogeneity of the trenches etched needs to be improved. Our future study will be oriented on the mechanism of potential barrier creation, further line-width reduction, and topographic homogeneity improvement. The technique presented is promising for the development of future nano-scale electronic devices operated both at low and high temperatures.

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