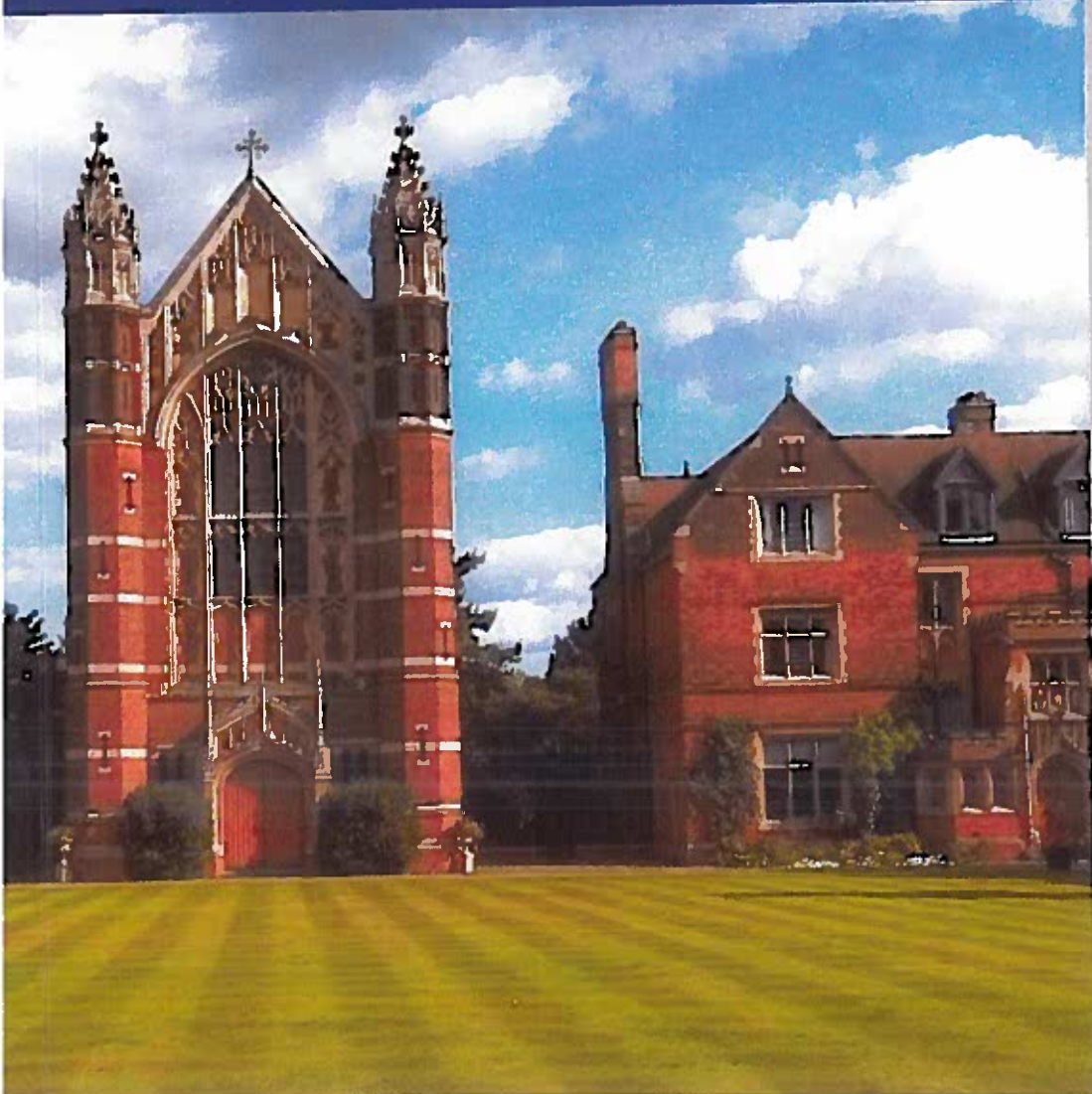




# International Quantum Cascade Lasers School and Workshop

Sunday 4 – Friday 9 September 2016  
Cambridge, UK



# Reactive Ion Etching of ZnO Epilayers for Resonant Tunneling Diodes and Quantum Cascade Structures

Borislav Hinkov<sup>1,2</sup>, Daniela Ristanic<sup>1</sup>, Werner Schrenk<sup>1</sup>, Maxime Hugues<sup>2</sup>, Jean-Michel Chauveau<sup>2</sup> and Gottfried Strasser<sup>1</sup>

<sup>1</sup>Institute of Solid State Electronics and Center for Micro- and Nano-Structures, TU Wien, Floragasse 7, 1040 Wien, Austria  
<sup>2</sup>Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre national de la Recherche Scientifique (CNRS-CNRS), Rue B. Gregory, F-06560 Valbonne Sophia Antipolis, France  
 borislav.hinkov@tuwien.ac.at

## 1. Introduction

The terahertz (THz) spectral range ( $\lambda \sim 30 \mu\text{m} - 300 \mu\text{m}$ ) which is located between the infrared and the millimeter-wave region is also known as the so-called "THz-gap", because of the absence of suitable compact semiconductor devices. Various real-world applications would strongly benefit from such sources, e.g. for trace gas spectroscopy and sensing, security screening and imaging, medical diagnostics and optical free-space communications.

A crucial step towards the utilization of devices for such kind of applications is the availability of small, compact and robust semiconductor sources that moreover can operate at room temperature. But this is out of reach with the currently available GaAs-based quantum cascade lasers (QCLs). They are limited in high-temperature operation towards room-temperature by the parasitic, non-optical low LO-phonon transitions (36 meV in GaAs) which are on the same order as the thermal energy at room temperature ( $kT = 26 \text{ meV}$ ). One possible solution is the use of materials with larger LO-phonon energy like GaN ( $E_{LO} = 91 \text{ meV}$ ) or ZnO ( $E_{LO} = 72 \text{ meV}$ ) to suppress the parasitic LO-phonon emission.

To master the fabrication of ZnO-based QC structures, i.e. QCLs (emitters) and QC detectors (QCDs, detectors), the epitaxial growth of such type of devices has to be mastered first. This also includes the following fabrication process which consists of surface-patterning and (selective) ZnO/ZnMgO etching steps, contact-deposition, surface-passivation of selective areas and annealing processes.

In this paper we present the first step towards the realization of ZnO-based QC-structures which is the reactive-ion based etching (RIE) of Ga-doped epitaxial layers and substrates of ZnO.

## 2. Device fabrication

The devices presented in this study were grown on m-plane (10-10) ZnO-substrate. One micrometer of Ga-doped ZnO was deposited on  $1 \times 2 \text{ cm}^2$  pieces of these substrates by molecular beam epitaxy (MBE).

In a next step a 1.3  $\mu\text{m}$  thick SiN hardmask was deposited by plasma-enhanced chemical vapor deposition (PECVD) on top of the epitaxial layer. It was patterned by photolithography and a following RIE step in a  $\text{O}_2$ -CHF<sub>3</sub>-based chemistry into square mesas with different sizes between  $50 \times 50 \mu\text{m}^2$  up to  $150 \times 150 \mu\text{m}^2$ .

The ZnO-etching was then performed based on a CH<sub>4</sub> process with a ICP-power of 200 W and a RF-bias-voltage of 500 V in an Oxford Plasmalab 100 RIE-reactor. The other parameters where: temperature  $\sim 30^\circ\text{C}$ , gas-flows of  $30/3/3 \text{ sccm}$  ( $\text{CH}_4/\text{H}_2/\text{Ar}$ ) and a chamber pressure of 20 mTorr. This process relies on the deposition of an amorphous carbon-layer on top of the hardmask to protect it, while the ZnO itself is etched continuously. In literature such a process was applied using regular photoresist as masking material, with slightly different gas-flow ratios and achieving up to infinitely high selectivity towards the resist mask [1].

In our experiments we also tested a 1  $\mu\text{m}$  thick Au-layer and 1.4  $\mu\text{m}$  thick resist as masking material, applying the same etching procedure as for the SiN. But both alternative hardmasks got etched away before reaching the wanted 10  $\mu\text{m}$  of etching depth. We therefore conclude that in our ICP-machine for the chemistry we use, the SiN-mask is the best choice.

Figure 1 shows the SiN-sample at three different stages of the device fabrication: a) before the etching, b) after 50 minutes of etching and c) after 140 min. Before the etching starts we can clearly observe some wavy roughness along the edges of the mesas. After the first etching step of 50 min, we can identify the 1.3  $\mu\text{m}$  of SiN hardmask (shiny), the 1  $\mu\text{m}$  of Ga-doped ZnO-layer (dark gray) and the 2  $\mu\text{m}$  thick etched ZnO substrate (light gray) in the profile of the mesa. The sidewall is vertical and no change in etching-profile is observed between epilayer and substrate. After 140 minutes of total etching time, a depth of 10  $\mu\text{m}$  is reached (etch-rate: 62 nm/min, selectivity:  $>> 1:30$ ).

We can clearly see in Fig. 1c) that the surface of the SiN is still undamaged and almost perfectly flat. On the sidewalls of the etching profile we can observe some roughness and inhomogeneity which is directly transferred from the SiN mask (see also Fig. 1a) and b)). In general the sidewalls are still completely vertical for all the crystal orientations. This is also expected since the dry-etching process in the RIE should be anisotropic and no crystal orientation should be etched faster. We expect that the rough surface and some of the roughness at the sidewalls can be removed by an additional (isotropic) wet-etching step, e.g. in a diluted HCl or  $\text{H}_3\text{PO}_4$  solution. Both etchants are known to etch ZnO significantly fast and will smooth out the ZnO surface and mesa sidewalls.

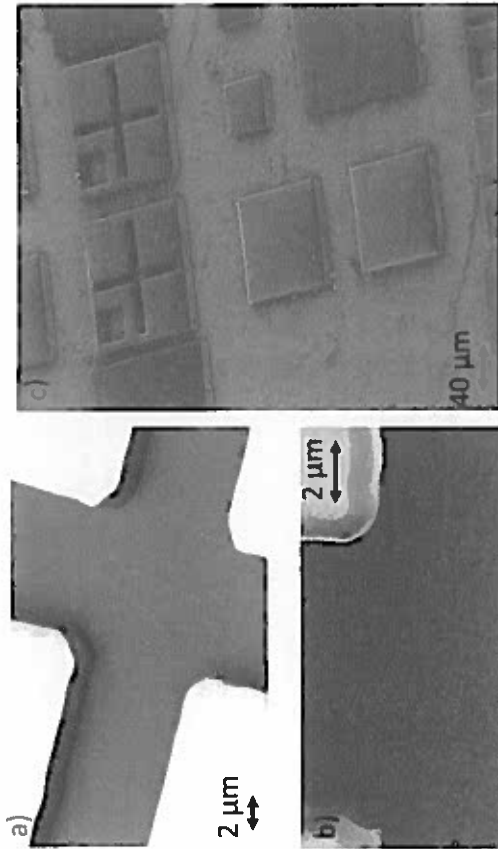


Fig. 1: a) ZnO with 1.3  $\mu\text{m}$  of SiN mask before RIE-etching. b) After 50 min of etching (recipe see text). Three layers can be identified in the etch-profile: the shiny still about 1.3  $\mu\text{m}$  thick SiN mask on top, the 1  $\mu\text{m}$  of Ga-doped ZnO-layer (dark gray) and the ZnO substrate underneath (light gray), 2  $\mu\text{m}$  thick. Total depth: 4.3  $\mu\text{m}$ . c) After final etching-step (total of 140 min) and a etching-depth of about 10  $\mu\text{m}$ .

## 3. Conclusion and Outlook

In conclusion we showed the RIE-etching of Ga-doped ZnO grown by MBE on m-plane ZnO substrate. Vertical sidewalls, reasonably fast etching (62 nm/min) and a very high selectivity towards a SiN-hardmask could be achieved ( $>> 1:30$ ). The observed roughness at the ZnO-surface and the sidewalls is expected to be smoothed-out by an additional wet-etching step in a diluted HCl or  $\text{H}_3\text{PO}_4$  solution.

In a next step towards the realization of QC structures, a study on resonant tunneling diodes (RTDs) with different parameters (one or two barriers, different dopings) will be performed and presented.

## 4. References

- [1] S.-W. Na, M. H. Shin, Y. M. Chung, J. G. Han, and N.-E. Lee, "Investigation of process window during dry etching of ZnO thin films by CH<sub>4</sub>-H<sub>2</sub>-Ar inductively coupled plasma", *J. Vac. Sci. Technol. A* 23, 898 (2005).