CH_4/H_2 Plasma Etching of IV-VI Semiconductors

Th. Schwarzl, W. Heiß, G. Kocher-Oberlehner, and G. Springholz

Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

We demonstrate for the first time CH_4/H_2 plasma etching of IV-VI nanostructures. Similar as for II-VI compounds, we find a power law dependence between the etch rate and the energy band gap. However, if other than group IV elements are incorporated in the crystal, the etch rate deviates from this behavior. In particular, for $Pb_{1-x}Eu_xTe$ the etch rates drastically decrease with increasing Eu content, which can be used, e. g., for preferential etching.

1. Introduction

The narrow gap IV-VI semiconductor compounds have major importance for the fabrication of mid infrared optoelectronic devices like lasers and detectors operating in the spectral range between 3 µm and 30 µm [1]. In the fabrication of such devices lithographic patterning and etching are of crucial importance. Up to now only wet chemical etching has been used for the fabrication of buried IV-VI heterostructure lasers. For III-V and II-VI semiconductors, however, it has been shown that plasma etching is superior in several aspects as compared to wet chemical etching. In this work we demonstrate for the first time the feasibility of CH_4/H_2 plasma etching for the structurization of IV-VI semiconductors.

2. Experimental Procedures

Our etching experiments are performed in a Technics Plasma PP300/M barrel reactor operating at 2.45 GHz. The samples are placed in the center of the reactor, which consists of a glass chamber with a total length of 40 cm and a diameter of 24.5 cm. The gas flow through the reactor is controlled by mass flow controllers for CH_4, H_2, and Ar, and the pressure is adjusted at about 0.3 mbar by a control valve to the vacuum pump. The typical steady state temperature of the samples during plasma etching reaches 150 °C. Prior to the etching, photoresist patterns are produced by standard photo lithography. Etch masks are obtained by depositing 500 Å to 1500 Å Cr on the photoresist and subsequent lift-off. For our etch experiments we use several micrometer thick molecular beam epitaxial PbTe, PbSe, and $Pb_{1-x}Eu_xTe$ layers grown on [111] oriented BaF_2 substrates. The etch process was characterized by a profilometer and by examining the etched profiles by scanning electron microscopy.

3. Plasma Etching of Different IV-VI Compounds

In a first set of experiments we etched several different IV-VI semiconductor compounds simultaneously in the barrel reactor. Thus, the process parameters (gas flows of

5 sccm CH_4, and 50 sccm H_2, 300 W rf power, 0.2 mbar pressure in the chamber) were identical for all samples. The achieved etch depths after 10 min etching time are shown in Fig. 1 as a function on the energy band gap for the binary compounds PbSe, PbTe, and PbS, revealing a systematic decrease of the etch rate with increasing band gap. The experimental data can be fitted by a power law:

$$\text{etch rate}_{IV\text{-}VI}\ [\text{nm/min}] = 50500\ E_{gap}[\text{eV}]^{-3.2} \qquad (1),$$

as demonstrated by the dashed line in Fig. 1.

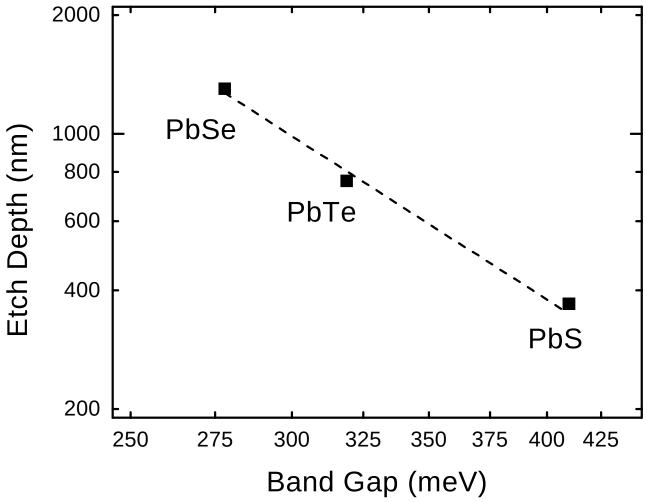

Fig. 1: Etch depth as function of band gap for binary IV-VI semiconductors achieved in a barrel reactor with 5/50 sccm CH_4/H_2 gas flow, 300 W rf power, 10 min etch time and p = 0.2 mbar. The dashed line represents a power law fit of the data.

A similar dependence is also valid for II-VI semiconductors. In our barrel reactor we achieved for CdTe, ZnTe, ZnSe, ZnS:

$$\text{etch rate}_{II\text{-}VI}\ [\text{nm/min}] = 7000\ E_{gap}[\text{eV}]^{-5.9} \qquad (2)$$

This suggests an equivalent etch reaction for IV-VI and II-VI semiconductors. For $A_{II}B_{VI}$ semiconductors the etch process was suggested to be [2]:

$$A_{II}B_{VI} + 2H + 2CH_3 \longrightarrow A_{II}(CH_3)_2 + H_2B_{VI} \qquad (3)$$

The H and CH_3 radicals are generated in the plasma [3]. However, the CH_3 radicals can also react to form a polymer deposit [4], so that deposition and etching are always competing processes. As a consequence, the etch rate depends strongly on the CH_3 content in the plasma. The assumption that the B_{VI} component is reacting with the hydrogen was supported by Auger spectroscopy on the etched surfaces [5]. The similar dependence of the etch rate on the band gap energy of II-VI and IV-VI compounds indicates that the reaction in equ. (3) describes also that of the IV-VI compounds just by exchanging A_{II} with A_{IV}. However, when Pb is substituted by other elements such as in ternary IV-VI alloys, the chemical reactions are altered. We find that the etch rate is strongly reduced and the power law dependence does not hold when Pb is partially replaced by Sn, Mn, or Eu.

4. Plasma Etching of $Pb_{1-x}Eu_xTe$

For more detailed investigations of the etching behavior of ternary IV-VI compounds we have focused on the PbTe/$Pb_{1-x}Eu_xTe$ system which is one of the important material combinations for IV-VI laser fabrication. In Fig. 2(a), the etch depth of PbTe and $Pb_{1-x}Eu_xTe$ (x = 1 %) is shown as a function of methane concentration.

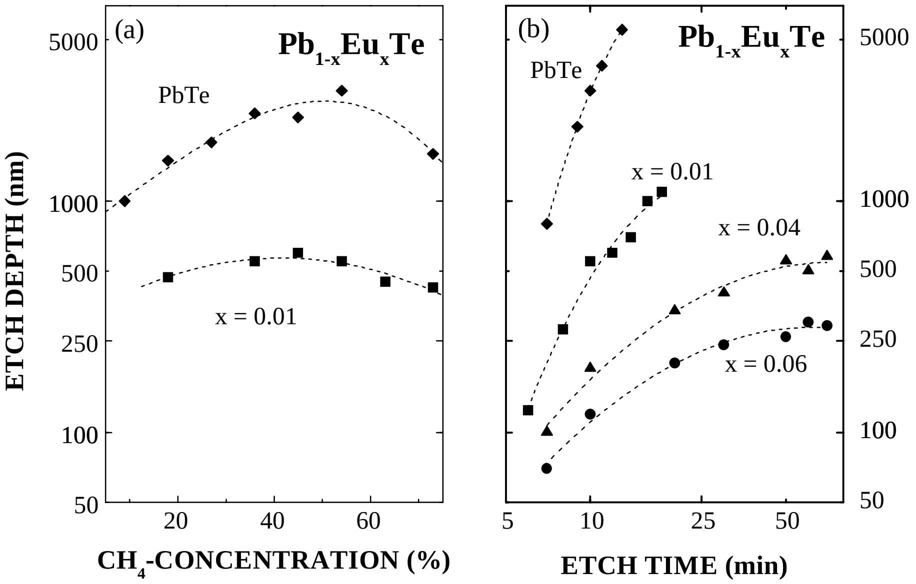

Fig. 2: (a) Etch depth of $Pb_{1-x}Eu_xTe$ after 10 min for a total gas flow of 55 sccm and an rf power of 300 W; (b) Time dependent etch depth for 30/25 sccm CH_4/H_2 gas flows. The dashed lines are guides for the eye.

These results are achieved with a total CH_4/H_2 gas flow of 55 sccm as optimized for this reactor and a rf power of 300 W. With increasing methane concentration the etch depth of PbTe after 10 min increases first from 1000 nm at 10 % CH_4 to 2600 nm at 54 %. Increasing the CH_4 content above 60 % leads to a decrease of the etch depth. This behavior indicates that the etch rate increases with the CH_3 content as long as no polymerization takes place. For PbEuTe (x = 1 %) a similar concentration dependence is observed. However, the etch rate is more than a factor of 3 lower than for pure PbTe and decreases drastically with increasing Eu content (see Fig. 2(b)). In addition the maximum etch rate shifts to lower CH_4 concentrations with increasing x_{Eu}. This could be caused either by polymer formation favored with increasing Eu content or by the formation of non-volatile Eu compounds.

This interpretation is further confirmed by our time dependent etching experiments as summarized in Fig. 2(b). In these experiments, a methane concentration of 54 % is chosen to give a maximum etching rate for PbTe, while the total gas flow and the rf power are the same as in Fig. 2(a). While for PbTe the etch rate is nearly constant in time, the etch rate of PbEuTe decreases more and more rapidly with time with increasing Eu concentration. In fact, for x_{Eu} = 6 % the etching stops completely after 60 minutes due to polymer or non-volatile Eu-compound formation. Fig. 2(b) also demonstrates the very strong dependence of the etching rate on the Eu concentration. For identical etch conditions, the etch depth decreases by a factor of 50 when x_{Eu} is increased from 0 % to 6 %.

Therefore, CH_4/H_2 plasma etching can be used as preferential etch to expose $Pb_{1-x}Eu_xTe$ heterojunctions.

Acknowledgements

We would like to thank O. Fuchs and M. Ratajski for technical assistance. This work is supported by the “Fonds zu Förderung der wissenschaftlichen Forschung, FWF, P12100-Phy”, Vienna (Austria).

References

[1] A. Katzir, R. Rosman, Y. Shani, K. H. Bachem, H. Böttner, and H. M. Preier, *Handbook of Solid State Lasers, ed. P. K. Cheo*, Marcel Dekker Inc. New York, 1989, p. 228

[2] A. Semu, L. Montelius, P. Leech, D. Jamieson, P. Silverberg: “Novel CH_4/H_2 metalorganic reactive ion etching of $Hg_{1-x}Cd_xTe$”, *Appl. Phys. Lett,*. Vol. 59, 1991, pp. 1752 – 1754.

[3] H. Toyoda, H. Kojima, H. Sugai: “Mass spectroscopic investigation of the CH_3 radicals in a methane rf discharge”, *Appl. Phys. Lett.*, Vol. 54, 1989, pp. 1507 – 1509.

[4] R. Cheung, S. Thoms, S. P. Beamont, G. Doughty, V. Law, C. D. W. Wilkinson: “Reactive ion etching of GaAs using a mixture of methane and hydrogen” *Electron. Lett.*, Vol. 23, 1987, pp. 857 – 858.

[5] M. Neswahl, K. H. Greßlehner, K. Lischka, P. Bauer, A. Brandstötter, K. Lübke: “Properties of dry-etched CdTe-epitaxial layer surfaces and microstructures”, *Materials Science and Engineering*, Vol. B16, 1993, pp. 108 – 112.