DEFECT-SELECTIVE ETCHING OF III-V AND WIDE GAP SEMICONDUCTORS

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ABSTRACT

The aim of this review is to present general characteristics of defect-selective etching and its position among other methods used for structural characterization of compound semiconductors. Two approaches to etching (orthodox and electroless methods) used for revealing and analysis of defects in GaAs, InP, GaN and SiC are described and critically evaluated. The importance of calibration of etching with direct high spatial resolution techniques is addressed.

1. INTRODUCTION

Wet chemical etching is one of the oldest methods used for characterization of single crystals. It was employed already in 19th century for defining the crystallographic orientation of natural crystals, though the users did not realize that etch pits were formed due to the presence of crystallographic defects. When in the fifties the correlation between the dislocations and pits was established, defect-selective etching became a routine and later standard method for defining the density of dislocations in semiconductor crystals. Due to the broad demand for quick and reliable characterization techniques for revealing defects and assessing the reasons for their formation, more sophisticated etching procedures have been developed, e.g. shallow photo-etching. As the result, apart of routine etch pit density (EPD) counting, it is possible to study the nature and origin of crystallographic and chemical inhomogeneities in bulk crystals, epitaxial layers and, in some cases, in the complete device structures. Following broad interest in this method and permanent progress in this field, numerous reviews continue to appear covering theory and practice of selective etching [1-7].

There are two characteristic features, which are inherent to any defect-selective etching method. The first one is based on the fact that the local differences in the etch rate are induced by the presence of crystallographic or chemical inhomogeneities but the defects are not directly visible and the chemical nature of inhomogeneities can not be defined solely by etching in a straightforward way. Therefore, selective etching has to be considered as an indirect method and, as a rule, calibration with other, preferably direct methods (e.g. Electron Microscopy) has to be used when new etches are introduced or when new material requires developing of a new etching system. This main drawback of selective etching is compensated by several advantages, such as inexpensive and simple equipment, short time of data acquisition, simplicity of experimental work, very broad range of defects which are revealed, practically no limit to the size of samples to be examined and the density of defects. Table 1 summarizes characteristic features of etching and of some core techniques commonly used for the structural study of semiconductor crystals and for calibration of etching.
The second factor, which for a long time put the limit on the resolving power (spatial resolution) of selective etching, is related to the choice of the post-etching method of examination of the etched surface. Conventional but unsophisticated optical microscope equipped with differential interference (DIC) and phase contrasts, yields the vertical resolution in the nanometer range. On the other hand, this method has rather poor spatial resolution (hundreds of nanometers). Scanning Electron Microscopy (SEM) allows one to examine the features with the size in the tens nanometer range but with the simultaneous loss of high vertical resolution characteristic of DIC optical microscopy. Remarkable progress in this field has been recently achieved by using near-field optical methods e.g. atomic force microscopy (AFM) for post-etching examination of the surfaces, which when employed after optimised etching procedures makes it possible to reveal nanometer size defects. Evidently recognition of the momentary changes of etch rate due to the action of etching medium on a defect site depends mainly on the actual resolution of the surface method used after etching.

Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of defect/range</th>
<th>Principle of image formation</th>
<th>Remarks</th>
</tr>
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<tbody>
<tr>
<td>X-ray topography</td>
<td>D: 0-10⁶, E</td>
<td>Bragg-reflection on lattice planes</td>
<td>Suitable for large area samples, N-D, expensive equipment, time-consuming</td>
</tr>
<tr>
<td>TEM</td>
<td>D, P: &gt; 10⁵</td>
<td>Diffraction/transmission of electrons according to Bragg’s law</td>
<td>Unique, direct information, resolution 0.2-5 nm, D, time-consuming, sophisticated equipment, expert operator</td>
</tr>
<tr>
<td>SEM-EBIC SEM-CL</td>
<td>Ch, D, P: 0-10⁶</td>
<td>Contrast due to radiative/non-radiative processes</td>
<td>EBIC: quantitative, partially D, time-consuming, CL: N-D, limited to samples with good CL efficiency</td>
</tr>
<tr>
<td>Etching+DIC/SEM/AFM</td>
<td>All defects</td>
<td>Selective chemical attack + surface method</td>
<td>Quick, simple, widely used, all sizes of samples, semi-D, indirect method</td>
</tr>
</tbody>
</table>

The theory and practice of defect-selective etching was well recognized and described for “classical” compound semiconductors such as GaAs and InP. For wide gap semiconductors, (especially GaN), the progress in defect-selective etching trailed behind the use of other methods of structural characterization (e.g. TEM), because of the high chemical resistance of this material and polarity-related strong anisotropy. In addition, the most commonly grown hetero-epitaxial GaN layers and structures contain dislocations of very high density (up to 10¹⁰ cm⁻²) and co-existing with dislocations specific type of defects, such as nano-pipes, pinholes and inversion domains. The combination of these factors makes it difficult to develop a reliable and universal defect-selective etching procedure. SiC bulk single crystals are characterized by much lower dislocation density, but micro-pipes, low angle grain boundaries and polytype lamellas are the common defects. Despite these unfavourable features of the wide gap semiconductors, large scale research performed recently resulted in introduction of different etching systems both for GaN and SiC. The aim of this presentation is to summarize the data on the defect-selective etching methods used for both III-V and wide gap materials and to emphasize their advantages and limitations.
2. PRINCIPLES AND CLASSIFICATION OF ETCHING METHODS

Wet selective etching proceeds via reactions that occur at the surface of the semiconductor. Consequently, the dissolution rate might be limited either (i) by the diffusion of the etching species towards the surface (or the diffusion of the reaction products from the surface) or (ii) by the rate of the reactions occurring on the surface. The first category is known as diffusion-limited (mass-transport-limited) etching and is used for removing work damages and morphological surface irregularity (e.g. hillock, protrusion). An ideal diffusion-limited etching solution results in flat and mirror-like surface, independently on the presence of crystallographic or chemical inhomogeneities in the etched material: the method is known as chemical polishing.

The second category covers defect-selective etching with the chemical activity of the surface as the rate limiting step (activation or kinetically controlled process), where selectivity refers to the local differences in the etch rate induced by structural or chemical inhomogeneities in the material. In this case the chemical activity of the surface, which for semiconductors depends on crystallographic, electronic and passivation effects, is the rate-limiting step.

There are two distinctly differentiated mechanisms of defect-selective etching of compound semiconductors. The first one, used mainly to reveal and assess the density of dislocations, is based on pure chemical etching, which occurs when during dissolution the bonds in the solid are broken and simultaneously replaced with the bonds to the component(s) of a reagent. During such chemical etching dissolution occurs preferentially at the outcrops of dislocations, see Fig. 1 a. Dislocation-related strain field (and in some cases the associated impurity atmosphere) is the reason for local increase of chemical potential, which is the driving force for nucleation and developing etch pits. The method is known as orthodox etching and, thought mainly used for EPD counting, yields some other valuable information on crystallographic orientation, decoration effects and geometry of dislocations. Broad description of thermodynamics- and kinetics-related conditions of pit formation in single crystals including compound semiconductors is given in [4,5,8].

The second mechanism operates in the etching systems (semiconductor-etch) where charge carriers are involved in dissolution. During this so-called electroless etching (no external potential is applied), two separate electrochemical reactions occur simultaneously on the semiconductor surface: reduction of an oxidizing agent, in which holes are injected into the semiconductor, and oxidation of the solid by the injected holes. The kinetics of this type of reaction is strongly influenced by the supply of carriers e.g. by illuminating the etched surface with light of a wavelength corresponding to the bandgap. In addition, due to recombination of photo-generated carriers at defects and inhomogeneities, selectivity of the electroless etching is remarkably increased. During electroless etching, complex etch features are formed at the defect sites, (non-crystallographic hillocks, ridges and/or depressions), but at the outcrops of dislocations always sub-micron protrusions are formed, as shown in Fig. 1b. The shape and extent of etch features depend on crystallography/geometry of dislocations and on chemical/electronic properties of the defects. More detailed description of these factors and
examples of etch features formed on defects in compound semiconductors during electroless etching are given in Sect. 2.2.

2.1. ORTHODOX ETCHING SYSTEMS AND EXAMPLES OF APPLICATION

Formation and growth of visible etch pits on outcrops of dislocations proceed via creation of stable nuclei (N in Fig. 1a) and their horizontal growth. Depending on the atomic-scale perfection of the steps (ledges), i.e. formation and kinetics of kink movement, either crystallographic or rounded pits develop. The former indicates the crystallographic orientation (symmetry) of the etched semiconductor surface. This fact is of particular importance for (001) surface of compound semiconductors, on which electronic devices are processed. The non-polar {001} faces in III-V compounds with zinc-blend lattice structure show polarity in the plane itself in <110> and <1-10> directions. For instance etching of GaAs (001) surface in molten KOH [5,9] yields pits, which are elongated in the [1-10] direction (Fig. 2a). Full correspondence between the elongated axis of the KOH etch pits and the crystallographic planes in the matrix occurs when the pits on the opposite sides of the etched wafer are formed under 90° angle, as illustrated in Fig. 2b (assuming the coordinate system, in which the (111) plane consists of group III (Ga) atoms). Preferential etching is, therefore, the simplest way to recognize these two non-equivalent directions and constitutes a standard method for defining orientation (OF) and identification (IF) flats used by III-V semiconductor substrates manufacturers.

Molten bases are also effective in revealing dislocations in wide gap materials. Pure KOH and KOH-NaOH eutectic alloy are used for studying defects in GaN and SiC [10-13]. Figs 3 a-b show some examples of the etch pits formed on dislocations in these semiconductors. Preferential etching of dislocations is also possible using concentrated or hot acids. Different etches were used for III-Vs and wide gap materials. Among the most popular are:

- Shell etch (aqueous HNO₃ solution [14]) for (111)Ga surface of GaAs;
- BCA etch (HBr-K₂Cr₂O₇-H₂O system [15]) for InP (see Fig. 3c);
- hot phosphoric and/or sulphuric acids for GaN [11,16].

The mechanism of etching of semiconductors in all these etches is purely chemical.
Fig. 3. SEM (a) and DIC optical images (b,c) of etch pits formed during etching of hetero-epitaxial GaN (a) and SiC single crystal (b) in molten KOH-NaOH eutectic and of InP single crystal in HBr water solution (c).

Fig. 4. (a) Hypothetical section profile of thickness of passivating layer $\theta$ formed on GaAs surface with emerging dislocation D, immersed in etching solution, which dissolves the semiconductor according to the electroless mechanism. SEM images of dislocations in n-type GaAs revealed by electroless dark- (b) and photo-etching (c).
2.2. ELECTROLESS ETCHING SYSTEMS AND EXAMPLES OF APPLICATION

During electroless etching of compound semiconductors, e.g. GaAs or InP in (CrO$_3$+ HF+H$_2$O) etch, the dominating role for defect-selective action is played by a passivating (adsorption) layer. The thickness of the passivating layer ($\theta$) constitutes the main factor which contribute to the final morphological characteristics of defect-related etch feature [17]. The deformation field around defects e.g. the strain field of dislocations reduces the Ga-As bond strength and by this increases locally the thickness $\theta$ of passivating layer (see Fig. 4a). As a result, during dark etching the outcrops of dislocations are revealed in the form of nano-meter size hillocks (tips), as shown by a scheme in Fig. 1b and SEM image of etched dislocation in Fig. 4b. Due to the nano-meter size of the tips of such hillocks, Scanning Electron Microscopy (SEM) seems to be the best tool for detailed examination of their size and morphology. When the same n-type material is etched under illumination, the overall etch rate increases considerably due to supply of photo-generated carriers and, at the same time, complex etch features are formed on the dislocation sites. Similarly to etching in the dark, at the outcrops of dislocations sharp summits are formed (see Fig. 4c), but now they reflect cylindrical region depleted in carriers due to their recombination at the very dislocation. The recombination process during photo-etching effectively increases defect-sensitivity as compared to dark etching. Shallow (sub-micron) photo-etching is usually sufficient in order to reveal clearly the presence of dislocations in n-type compound semiconductor. In addition, photo-etching discloses the presence of electrically active impurities around dislocations (see Fig. 4c). These atmospheres are revealed as either hillocks or depressions depending on their electronic nature and the type of etched semiconductor.

The most versatile DSL etching system for III-Vs has been used both for GaAs and for InP with white light and He-Ne laser illumination [5,6,17]. For photo-etching of GaN and SiC water solution of KOH and UV illumination are used to reveal dislocations and planar defects. Some examples of photo-etched materials are shown in Fig. 5a-b.

![Fig. 5. Defects (stacking faults and partial dislocations) in SiC single crystal (a) and in hetero-epitaxial GaN layer (b) revealed by photo-etching in aqueous KOH solution under Xe lamp illumination. (a) DIC optical image, (b) SEM image. In (c) cross-sectional TEM image of the GaN hetero-epitaxial layer from (b) demonstrates a one-to-one correlation between the etch whiskers and dislocations.](image)
One of the most important virtues of the electroless-type of selective (photo-)etching is that the dislocations are preserved inside etch hillocks which might be advantageous over the formation of pits during orthodox etching, especially when subsequent calibration with other structural or physical method is necessary. This virtue of photo-etching has been used recently for direct TEM calibration of etch features formed on high-dislocation density hetero-epitaxial GaN layers [18,19]. The cross-section TEM image of photo-etched sample confirms association of the whiskers with dislocations, as shown in Fig. 5c. This method is particularly attractive for material with very high density of defects (in the range $10^9$-$10^{11}$ cm$^{-2}$), in which overlapping of etch pits occurs during orthodox etching.

2.1. References