Formation of Abnormal Etch Pits on (111)_P Surface of n-GaP Crystal

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When (111) wafers of Te-doped GaP were etched in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio) at a temperature above 70°C for a period longer than 3.6×10^3 s, abnormal etch pits of asymmetric shape formed on the (111)_P surface in minor density compared to those of normal triangular pits and spiral pits. From microscopic observation, the abnormal pit had an etch beak projecting from its apex. In order to clarify the origin of abnormal etch pits, structural defects in the wafers were examined by transmission electron microscopy after thinning. As a result, they were classified into several types such as dislocations, dislocation loops, precipitates and lineage defects composed of a dislocation bundle. As the lineage defects often take such a peculiar configuration as a zigzag pattern, we suppose that the abnormal etch pit with a beak would nucleate owing to preferential dissolution along the lineage defect.

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1. Introduction

It is well known that the appropriate etching of a low-index surface of a crystalline material develops etch pits at locations on the surface intersecting with dislocations. In most cases, etch pits take a pyramidal shape which reflects the crystallographic symmetry of an etched surface. On the contrary, asymmetric etch pits called abnormal ones¹⁾ rarely form on a specific crystal surface: their origin is not always the same but a specific structural defect depending on the kind of crystals.

Recently, one of the authors, Sugawara,²⁾ found that abnormal etch pits nucleated in minor density among normal triangular pits and spiral pits by etching a (111)_P surface of n-GaP for a period longer than 3.6×10^3 s at a temperature above 70°C in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio). From a double etching technique, it was concluded that a triangular pit and a spiral pit corresponded to an edge dislocation and a screw dislocation, respectively. However, the origin of an abnormal etch pit has been unknown.

In this study, after inspecting the microscopic morphology of an abnormal etch pit forming on the (111)_P surface of an n-GaP wafer, we will show typical structural defects observed in thinned crystals by transmission electron microscopy and then will discuss the origin of an abnormal etch pit on the basis of morphological features of the defects observed.

2. Experiments

A sample of (111) wafers which were cut out from a liquid encapsulated Czochralski (LEC) GaP crystal, doped with Te at a concentration of 4×10^{23} atoms/m³, was kindly supplied by Sin'etsu Semiconductor Ltd.: their size was 47 mm in diameter and 0.35 mm in thickness. The wafers were cleaved along (110) directions into small specimens of a triangular shape with 7 mm in edge length. After being cleaned in acetone for 300 s with an ultrasonic cleaning equipment, specimens were etched in a solution composed of 97% $\text{H}_2\text{SO}_4 + 30\% \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio, 80°C) for a pe-

riod longer than 3.6×10^3 s. The microscopic morphology of abnormal etch pits forming on a (111)_P surface was examined by use of a scanning electron microscope (SEM; JEOL, JXA-733) and a transmission electron microscope (TEM; JEOL, JEM-2010): Pt-20%Pd shadow-carbon coating replicas were prepared by a conventional two-stage technique³⁾ for the observation of surface topography with the TEM.

Moreover, in order to clarify the origin of an abnormal etch pit, structural defects contained in n-GaP were studied with the TEM. Procedure in preparation of thin crystals was as follows. First, the as-etched specimens were cut into a smaller piece of a square shape with 3 mm in edge length by the use of a diamond wheel, so that an abnormal etch pit might locate approximately at a center of the (111)_P surface. Subsequently, the (111)_{Ga} surface was polished mechanically in order to thin a specimen to a thickness of less than 0.2 mm, and a depression was produced at a center of the (111)_P surface with a dimpling apparatus (Gatan, Model 656N). Further, surfaces of a specimen were milled by bombarding Ar ion at an accelerating voltage of 2–3 kV in an ion-beam thinning device (Gatan, Model 600DIF) until it was thin enough to be observed. After being fixed in a side-entry and single-tilt holder, the thinned specimen was investigated with the TEM operated under an accelerating voltage of 200 kV.

3. Results and Discussion

3.1 Microscopic morphology of abnormal etch pit

Figure 1 shows a typical micrograph of an abnormal etch pit,²⁾ which formed on a (111)_P surface of Te-doped GaP by etching in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio, 80°C) for 6.0×10^3 s. The abnormal pit is dark except for central region and large as compared with neighboring normal pits: it is pointed out that dark periphery and light center inside the abnormal pit correspond to steep lateral faces and gentle ones, respectively. However, their detailed morphology has been unknown, and hence microscopic observation by electron microscopy is required to examine it.

Fig. 1 Optical micrograph of an abnormal pit²⁾ formed on a (111)_P surface of Te-doped GaP by etching in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio, 80°C) for 6.0×10^3 s.

Fig. 2 (a) Scanning electron micrograph of an abnormal etch pit with a beak at an apex and (b) replica electron micrograph of an etch-beak. Etching of a (111)_P surface of Te-doped GaP was carried out in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1 in volume ratio, 80°C) for 6.0×10^3 s.

Figure 2 shows electron micrographs of abnormal etch pits. From a scanning electron micrograph (Fig. 2(a)) it is found that the abnormal pit has an etch beak projecting obliquely from its apex and that its lateral faces are composed of six curved facets which have a gentler slope near the apex. The crystallographic direction of a projecting beak is not always definite. On the other hand, the periphery of a beak appears light in contrast to the interior, which is caused by a quantita-

tive difference of detected secondary electrons depending on a geometrical arrangement between an elongated facet composing a beak (as mentioned below) and an electron collector of the SEM. Further, a replica electron micrograph (Fig. 2(b)) indicates that an etch beak takes flattened shape of about 20 μm in length and 10 μm in width and that it is also composed of somewhat curved and narrow facets extending over the whole projection. The authors consider that the formation of an abnormal pit with a beak may originate in preferential dissolution along a peculiar defect.

3.2 Structural defects observed in n-GaP crystal

A variety of defects observed in Te-doped GaP with the TEM are illustrated in Fig. 3: they are classified into dislocations, dislocation loops, precipitates and lineage defects composed of a dislocation bundle. Figure 3(a) shows a dislocation partially decorated with precipitates. It is considered that the precipitates are composed of doped Te atoms. However, we have failed in their identification with an X-ray energy-dispersive spectrometer (XEDS; Noran Instr., Voyager II) attached to the TEM, probably owing to their small content.

Figure 3(b) shows a helical dislocation and a dislocation loop. Similar configuration was found in S-doped (3.8×10^{23} atoms/m³) GaP by Dupuy and Lafeuille.⁴⁾ They considered that absorption of super-saturated interstitials by a screw dislocation led to the formation of a helical dislocation and that pinching-off of edge dipoles of a helix resulted in the formation of a dislocation loop. In the present study, these kinds of lattice defects appears rarely, probably because the density of screw dislocations is not very high in the GaP wafers used.²⁾

In addition to the above perfect loop, a faulted dislocation loop shown in Fig. 3(c) is present with a very low frequency. According to Ball and Hutchinson,⁵⁾ a similar faulted loop involved in S-doped (2×10^{24} atoms/m³) GaP was extrinsic in nature. They reported that the principal defect structure in the as-grown crystal consisted of dislocation clusters (including dislocation lines, helices and loops) and colonies of precipitates.

Under the present observation, many precipitates are often nucleated around dislocations as described above and are dispersed in the matrix as shown in Fig. 3(d), forming a colony. In the photo, dispersed precipitates are seen as dark dots or a triangular particle from which a dislocation bows out. Ball and Hutchinson⁵⁾ analyzed detailed morphology of such a polygonal particle also by tilting experiments, although its chemical composition was not identified with an XEDS system. As a result, they concluded that a polygonal particle actually took the shape of a tetrahedron surrounded by {111} facets.

On the other hand, Fig. 3(e) shows a lineage defect composed of a dislocation bundle. The defect often takes a peculiar shape of a zigzag pattern: that is, a horizontal line in strong contrast parallel to a $\langle 211 \rangle$ direction, and a vertical part of a dislocation array showing faint contrast. Such a peculiar defect composed of a dislocation bundle has not been found in GaP hitherto as far as we know.

Fig. 3 Typical transmission electron micrographs of a variety of defects contained in (111) thin crystals of Te-doped GaP. (a) Dislocation partially decorated with precipitates, (b) helical dislocation and dislocation loop, (c) faulted dislocation loop, (d) dispersed precipitates and (e) lineage defect composed of a dislocation bundle. A symbol g used in the photos represents a diffraction vector.

3.3 Origin of abnormal etch pits

As already mentioned (III.1), an abnormal pit with a beak as well as a normal triangular pit and a spiral pit are formed on a (111)_P surface of n-GaP etched with $H_2SO_4 + H_2O_2 + H_2O$ (5 : 1 : 1, 70–80°C) for a period longer than 3.6×10^3 s. According to Sugawara,²⁾ the normal pit and the spiral pit in the above pits correspond to an edge dislocation and a screw dislocation, respectively. Although Amelinckx *et al.*⁶⁾ expected that a spiral pit might nucleate at a helical dislocation as shown in Fig. 3(b), many investigators⁷⁾ have insisted on a one-to-one correspondence between a spiral pit and a screw dislocation in some kinds of crystalline materials other than GaP also. Until now it is unknown what type of a pit occurs at a helical dislocation, nevertheless, a helix does not seem to be responsible for the formation of a beaked pit as the defect

is nothing but a spiral prismatic dislocation.⁸⁾

On the other hand, Iizuka⁹⁾ pointed out that small defects such as isolated precipitates, vacancy aggregates or dislocation loops were revealed as shallow and flat-bottomed pits (S-pits) composing a cluster in a dislocation-free region when etching was carried out on a (111)_P surface of n-GaP with a dislocation etchant such as Abrahams and Buiocchi's etch¹⁰⁾ (AB etch), or Richards and Crocker's etch¹¹⁾ (RC etch). In the present etching no S-pit forms, and the small defects as shown in Figs. 3(c) and 3(d) never appear as beaked pits because the size of these defects is too small in comparison with the length of a beak (about 20 μm).

On the contrary, the lineage defect shown in Fig. 3(e) takes a peculiar configuration. As composed of a dislocation bundle, the defect has larger strain energy than a single dislo-

cation. Thus, under dislocation etching faster dissolution is anticipated to occur along the lineage defect, followed by the formation of a rather large pit with steeper lateral faces in comparison of a normal pit. In addition, as the defect often bends sharply at some intervals, intermittent and preferential dissolution along a specified direction of the zigzag defect will make it possible to develop a flat-bottomed and eccentric pit with a beak.

4. Conclusions

After the (111)_P surfaces of Te-doped GaP were etched in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ (5 : 1 : 1, 80°C) for a period longer than 3.6×10^3 s, the microscopic morphology of an abnormal etch pit showing an asymmetric shape was examined by electron microscopy. The abnormal pit has an etch beak at the apex, which projects obliquely toward an indefinite crystallographic direction. Moreover, an etch beak takes flattened shape of about 20 μm in length and 10 μm in width and it is composed of curved and narrow facets extending over the whole projection.

Further observation of structural defects contained in thinned GaP was made with the TEM. They are classified into dislocations, dislocation loops, precipitates and lineage defects composed of a dislocation bundle. Among them the lineage defect takes a peculiar shape of a zigzag pattern, and

it is assumed that the eccentric pit with a beak at an apex will develop if intermittent and preferential dissolution proceeds along a specified direction of the zigzag defect.

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