ECR RIE-Enhanced Low Pressure Plasma Etching of GaN/InGaN/AlGaN Heterostructures

Bedwyr Humphreys, Matthew Govett
Oxford Instruments Plasma Technology

Abstract

A room temperature (RT) plasma etch process has been developed to non-selectively etch GaN/InGaN/AlGaN structures, grown on sapphire substrates, using an electron cyclotron resonance (ECR) plasma source with RIE enhancement. The process chemistry chosen was Cl_2/CH_4 based in order to facilitate the formation of volatile etch by-products, typically to form group III halides and group V hydrides, although indium is more likely to form an organo-metallic compound as opposed to a chloride. A characteristic of this process is the very smooth sidewall features obtained and the controllability of the etch profile via ECR power, table bias and/or gas flow ratio. Typical results obtained using a RT process were etch rate above 100 nm/min., selectivity to resist mask above 30:1 and smooth anisotropic profile at low ion-energies (below 100 eV). The process etch rate showed a characteristic increase with increasing table bias (above 130 nm/min.) with only small changes in the relative etch rate of each compound (i.e. selectivity maintained at roughly 1:1), however, this etch does rely upon competing etching and deposition mechanisms and thus too large a variation in one parameter without a corresponding compensation with another leads to a rough surface and a more selective etch. The process has also been demonstrated using a metal mask (e.g. Ni) and present work is progressing onto other gas combinations and the use of high temperature electrodes.

1. Introduction

A great deal of interest has recently been shown in GaN and its related ternary compounds especially since the fabrication of the first GaN based semiconductor laser diode operating at room temperature (RT) by Nichia Chemical Industries. The active region consisted of $In_{0.2}Ga_{0.8}N$ quantum wells separated by $In_{0.05}Ga_{0.95}N$ barriers, formed between $Al_{0.15}Ga_{0.85}N$ cladding layers and stimulated emission was seen at 417 nm under RT pulsed conditions [1].

GaN based materials are highly attractive for use in optoelectronics because of their wide direct bandgaps, the potential bandgap range simply between GaN and AlN is 3.4 eV - 6.2 eV. The use of such wide bandgap materials offers the potential for devices operating in the ultraviolet and at even shorter wavelengths, such devices would dramatically increase the potential storage capacity of optical disks due to the sharper focusing of the shorter wavelength blue laser, compared to the currently available commercial lasers.

Other uses of GaN based compounds are as insulators because of their high dielectric constants and GaN has been used as an insulator in metal-insulator-semiconductor (MIS) devices grown on GaAs [2]. High electron mobility has also been reported, which makes GaN a very attractive material for high speed device applications [3].

Typical material growth techniques used to date for the III-V nitrides were MBE, MOVPE and plasma enhanced MBE onto suitable substrate materials such as sapphire, ZnO or SiC. Although, working devices are now being fabricated using GaN based materials, many problems still exist with the growth processes which result in high dislocation densities at the substrate interface due to a 15% lattice mismatch, i.e. material quality far worse than typical GaAs based growth. Other problems which still complicate and influence device fabrication yield are poor contact formation to the nitrides (both ohmic and Schottky) and limited etching capabilities due to the relatively inert nature of the III-V nitrides during wet etch. A number of dry etch process techniques have been investigated with the majority of the initial work being carried out using standard GaAs based etchants (BCl_3 or $SiCl_4$) in a reactive ion etch

majority of the initial work being carried out using standard GaAs based etchants (BCl$_3$ or SiCl$_4$) in a reactive ion etch (RIE) parallel plate plasma. These processes tended to be relatively slow and etching was generally dominated by ion bombardment resulting in a reactive sputter etch [4], [5]. Other researchers have approached the problem from a different perspective whereby the basic requirements for a successful dry etch process were addressed. In order to efficiently remove the etch layer, it is desirable to form volatile etch by-products for all the elements concerned. Thus in the case of GaN, a chlorine based chemistry is suitable for removal of the group-III gallium (e.g. BCl$_3$ or SiCl$_4$) by formation of the volatile group-III chloride, but does not address the problem of forming a volatile group-V etch by-product. Addition of fluorine in the form of SiF$_4$ has been investigated in an attempt to form a volatile group-V fluoride e.g. NF$_x$, but additions of SiF$_4$ to a SiCl$_4$ based plasma did not increase the GaN etch rate [6]. Possibly, this reaction mechanism is thermodynamically "uphill» or the formation of involatile GaF$_x$ impedes the chemical reaction.

More recent work has concentrated on removal of the group-V nitride component via formation of a volatile hydride compound. This reaction mechanism proved to be very successful and material etch rates were seen to increase upon the addition of hydrogen or a hydrogen containing gas to the plasma. Additionally, a shift towards high density plasma (HDP) was made which further opened up the possibilities of high rate low damage etching [7], [8].

This paper describes plasma etching results obtained for GaN, InGaN and AlGaN materials grown on sapphire substrates using a HDP electron cyclotron resonance (ECR) source with a separate RF biased electrode using a Cl$_2$/CH$_4$/Ar process.

2. Experimental

All samples provided were grown on sapphire substrates and a schematic of the layers provided is shown below in Figure 1. The GaN only pn junction structure was patterned with a positive photoresist mask whereas the GaN/AlGaN/InGaN heterostructure was patterned using a Ni/SiO$_2$ mask.

It is not clear what growth technology was used for the structure preparation and what concentration of dopant was present within each layer. The thicknesses provided were also approximate. The masks used were again not chosen for any specific reason, with regards to the etch, but it is interesting to note that the final etch results do not suffer as a consequence of using different mask materials.

The plasma etch system used for the etching experiments was an OXFORD Plasma Technology PlasmalabSystem 90 fitted with an Astex 4555 single magnet ECR head with a 700W 2.45 GHz microwave generator. The microwaves were generated in a magnetron source and were channelled to the ECR chamber via waveguides. A three stub tuner and a three port power circulator were located between the magnetron source and the ECR head in order to facilitate tuning of the microwaves and to prevent reflected microwaves from entering back into the magnetron, respectively. ECR also requires the use of a magnetic field in order to create electron resonance. The magnetic field required for resonance to occur at a frequency of 2.45 GHz is 875 Gauss, and in this case the field was supplied via an electromagnet situated radially around the quartz cavity.The hardware configuration used also utilised an RF biased 275 mm aluminium electrode upon which the samples were placed via a quartz coverplate. Separating the plasma ion density control (ECR) from the plasma ion energy control (RF bias) results in a highly controllable etching process whereby high density (10^{11} - 10^{12} cm^{-3}) high rate processes at low ion energy (low eV) are achieved. An additional benefit of using ECR is its low operating pressure, typically ~1 mT, which results in very high ion mean free paths (at low energies) which ultimately dictate the angle at which an ion impacts the wafer surface, hence further enhancing the anisotropy of the etch. Operating at such low pressures in a standard RIE chamber would drastically reduce the plasma density and greatly increase the ion energy, totally opposite to the desired effect.

The pumping configuration used to achieve the low processing pressures demanded by ECR was a 360 l/sec Leybold turbomolecular pump backed with an Edwards E2M40, the process chamber being pumped by this combination via a 150 mm diameter pumping port. The base pressure achieved for this load locked chamber was <5 x 10^{-6} Torr and chamber leak rate was <1 mT/min. The advantages of using a load locked turbo pumped process chamber are effective removal of water and oxygen contamination, which ultimately results in excellent run to run reproducibility. The hardware configuration is shown below in Figure 2.

The samples (typically 1 cm^2) were placed on the quartz coverplate in the loadlock and once the loadlock had been pumped to a suitable vacuum, the coverplate was automatically transferred into the process chamber. The onset of processing was delayed until the process chamber reached a base pressure of < 8 x 10^{-6} Torr in order to maintain run reproducibility. The table was situated approximately 25 cm downstream from the ECR cavity, moving the table closer to the ECR cavity would increase the process etch rate (due to the increase in plasma density), but would

also detrimentally affect the across table uniformity. No additional magnets were used for shaping the downstream plasma, which would also increase plasma confinement but additionally improve the across electrode uniformity. However, this additional hardware was not deemed necessary at this stage of the process development. Gases were all introduced into the ECR head and thus were all highly ionised, it is also possible to separate the gases so that some gases flow into the head and others into separate gas ring located down stream from the ECR cavity.

3. Results

In order to facilitate gaseous removal of both the group III chlorides and the group V nitrides, a chlorine/methane (Cl_2/CH_4) process was chosen. In addition to these two gases, argon (Ar) was also added to stabilise and enhance plasma uniformity. All processing was carried out at room temperature, but recent research has shown that etch rates for both InN and GaN increase with increasing temperature and decrease for AlN when a Cl_2/CH_4/H_2/Ar process was used [7]. The choice of RT processing was made, however, due to the expectation that effective formation of volatile etch by-products would occur at RT under the low pressure conditions used.

The starting etch parameters were 10 sccm Cl_2, 2 sccm CH_4 and 10 sccm Ar. This was a process chemistry which had proven to be an effective ECR etch for InP and its associated quaternaries at RT using only moderate RF bias. The results from this etch using the resist masked GaN pn junction samples is shown below in Figure 3. As can be seen from the SEM, the profile is sloped at approximately $60°$ to the horizontal and the underlying surface of the sapphire substrate can be seen to be pitted. The sloped profile can be attributed to mask recession and thus a reduction in the dc bias or an increase in the methane flow to increase mask polymerisation should result in a more vertical sidewall profile. The etch rate of this process was approximately 135 nm/min. with negligible etch rate non-uniformity across the 1 cm^2 sample. The pitting seen in the sapphire substrate can possibly be attributed to a combination of ion bombardment and localised adsorption of HCl on the sample surface during the overetch step. Using the same process as above, but decreasing the dc bias from 140 eV to 95 eV resulted in a much more vertical etch profile, but at the expense of etch rate which was reduced to approximately 100 nm/min.. The resist mask selectivity for this second process was calculated to be greater than 30:1.

Although ion energy had been reduced to below 100 eV, there were still signs of pitting in the sapphire substrate (sapphire not GaN as a 100% over etch was used to clear the layers). Therefore, it appears that the pitting is more susceptible to attack by chemical etching of the surface via adsorption of HCl species on the surface, this reaction, however, is almost certainly enhanced by ion bombardment.

It was also expected that ECR power would have an effect on sidewall profile angle due to the relative increase or decrease of the polymerising component with respect to the etching component. This was investigated using the second set of samples using similar process conditions to those used for the GaN pn junction etch. The first process used was carried out at the same process conditions as those of Figure 4, the reason for this being to compare the etch results for different masks. This process would also provide results to whether the ternary layers, InGaN and AlGaN, etched at a similar rates to the GaN.
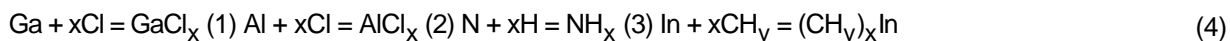
Figure 5 below shows the resultant profile from the etch carried out on the heterostructure samples, again the sample size was approximately 1 cm^2. The process conditions used were as follows: Cl_2 = 10 sccm, CH_4 = 2 sccm, Ar = 10 sccm, pressure 1 mT, DC Bias = -95 V, ECR Power = 400 W.

As can be seen from the SEM photograph, a highly anisotropic process was achieved which resulted in a positively sloped etch profile. Close inspection of the sidewall surface shows very little indication of selectivity to the individual layers although heavy vertical striations can be seen due to poor mask integrity. The highly anisotropic nature of the etch results in a profile which exactly follows each mask edge non-uniformity. The lack of horizontal striations present in the sidewall profile indicates the low selectivity achieved between the ternary layers and the GaN, hence this implies that all layers etch at comparable rates. Close inspection of the foot of the etched feature also reveals a trench around the edge of the feature, this type of effect has been observed previously during InP etching under similar conditions and is attributed to reduced polymer formation on and around the mask and the etched sidewall due to a reduction in the neutral/ion ratio at the feature edges. This can be compensated for by producing more polymer forming neutrals. Therefore addition of methane or production of increased polymer sources should decrease the trenching effect and also improve the verticality of the etch. The etch depth for this etch, as measured by a Tencor α-step profilometer, was ~ 3.5 μm which corresponds to an etch rate of approximately 100 nm/min.. This result indicates that under the process conditions used, the etch rates of AlGaN, InGaN and GaN are very similar and equate to approximately 100 nm/min.. The notching seen directly beneath the mask at the mask-semiconductor interface is due to undercutting of the silicon dioxide beneath the nickel mask. The oxide was wet etched using the nickel mask prior to dry etch processing of the semiconductor layers.

Figure 6 below shows the effect of increasing the ECR power from 400 W to 700 W on sidewall profile and as can be seen from the SEM photograph, the sidewall profile has become almost vertical, with again no indication of horizontal striations. There is, however, still evidence of trenching to be seen at the foot of the feature, but this is much improved from the previous case and would be eliminated at higher powers. Conversely, further additions of methane should also serve to eliminate this trench from the foot of the features.

The etch depth in figure 6 was approximately 3.5 μm which corresponded to an etch rate of 110 nm/min., thus an increase in ECR power increases the overall etch rate by increasing the plasma density, but at the same time increases the polymerisation component which limits the degree of trenching. Increased methyl reactant groups also increase the likelihood of removal of indium and therefore will also aid in shifting the etch profile from positively sloped towards the vertical.

Although the process used has been shown to have a relatively wide process window (large power variations being shown to affect sidewall profile), it still relies heavily on the fine balance between competing etch and deposition processes. The expected etching mechanisms of this process are polymerisation of C-H species on all surfaces within the reactor, followed by sputter removal from the electrode by a combination of argon and chlorine ions. Sputter removal will be the only mechanism for removal of this film from the masked areas of the sample, but sputter induced chemical desorption will also occur on the semiconductor surface. The proposed etch mechanisms for formation of the volatile by-products are as follows.

$$Ga + xCl = GaCl_x \text{ (1)} \quad Al + xCl = AlCl_x \text{ (2)} \quad N + xH = NH_x \text{ (3)} \quad In + xCH_y = (CH_y)_x In \qquad (4)$$

It is also possible that Ga and Al will form methyl compounds as well, but plasma diagnostic techniques were not available during the work to confirm this.

Other researchers have shown that additional H_2 also enhances reaction (3) and results in an increase in the process etch rate, however, this processing was carried out at high temperature and in a methane free environment [7]. Therefore, it was not deemed necessary to add additional hydrogen to the process although greater process versatility would be achieved.

Other possible etch chemistries suitable for etching the above layers are a high temperature methane free process using $Cl_2/H_2/Ar$ or a room temperature $HBr/Cl_2/H_2/Ar$ process. The former relies on removal of the etch layers according to the above reaction mechanisms (1) to (3), but removal of indium relies on the formation of $InCl_x$ which is only volatile at temperatures above 130°C, hence the need for a heated electrode. The latter process relies again on reactions (1) to (3), but indium removal is achieved via formation of volatile $InBr_x$ (volatile at room temperatures). Further investigation into these process chemistries was not possible due to a lack of suitable samples.

4. Summary

In summary, ECR RIE-enhanced etching of GaN/InGaN/AlGaN structures has been demonstrated using a $CH_4/Cl_2/Ar$ chemistry. Profile control was demonstrated as a function of ECR power (gas flow ratio) and dc bias using different masking materials. Differences were seen in the resultant profiles for different masks, but process compensation was possible in order to produce vertical profiles for all masks. The process relies on competing etch and deposition processes and profile control is as a direct consequence of altering the etch:deposition ratio. The etch rates of GaN, InGaN and AlGaN were deemed to be comparable due to the lack of horizontal striations on the sidewall profile, typically non-equal etch rates result in layer undercutting or overcutting. Etch rates of greater than 100 nm/min. were achieved on all samples at relatively moderate bias levels (below 100 eV) using 1 cm^2 samples. Further work will continue in the investigation of a RT methane free process.

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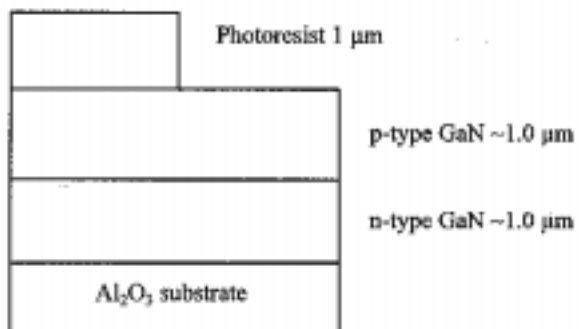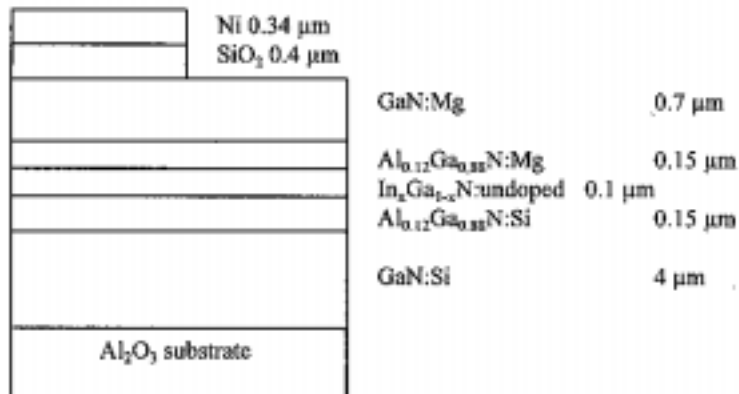
Figure 1. Heterostructure of the samples used for etching.

Figure 1
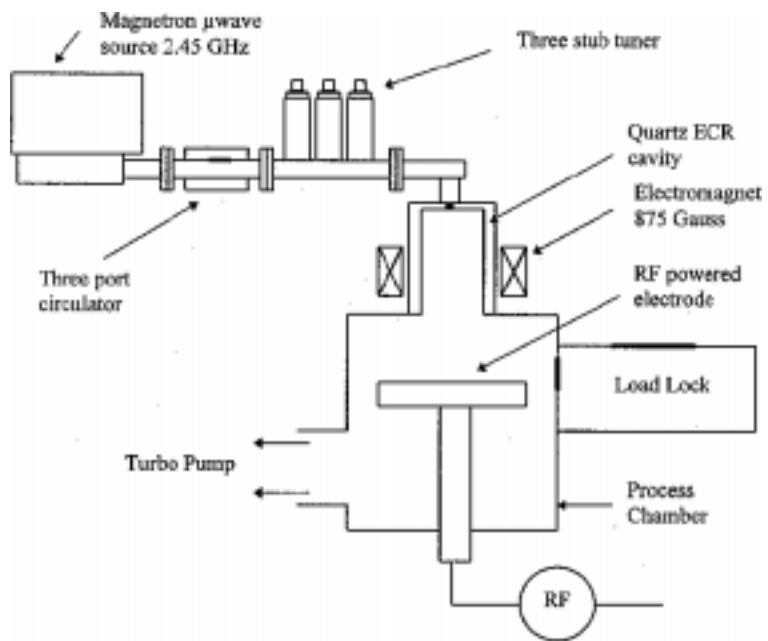
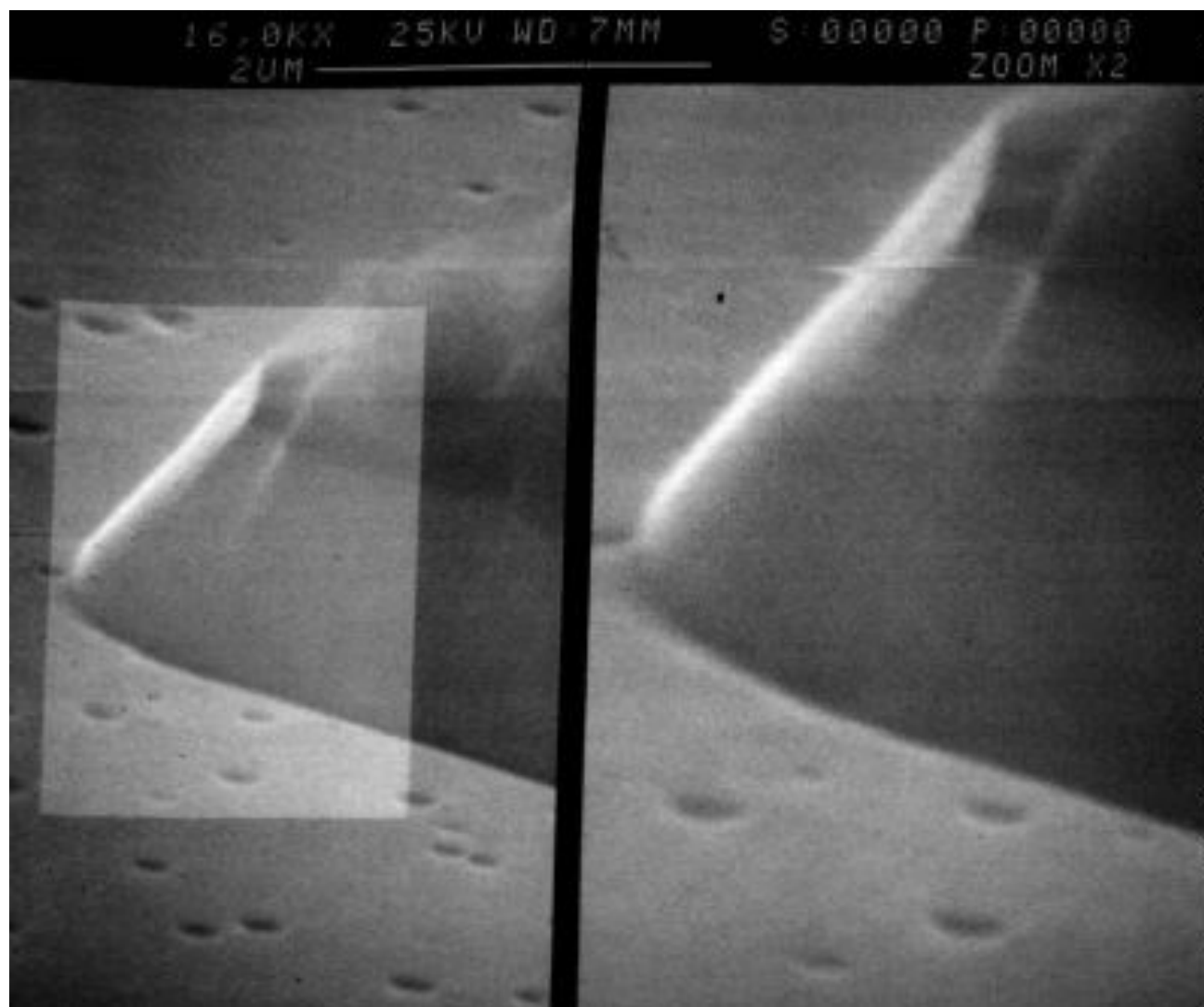**Figure 2**. Hardware schematic of the Oxford ECR system used for etching

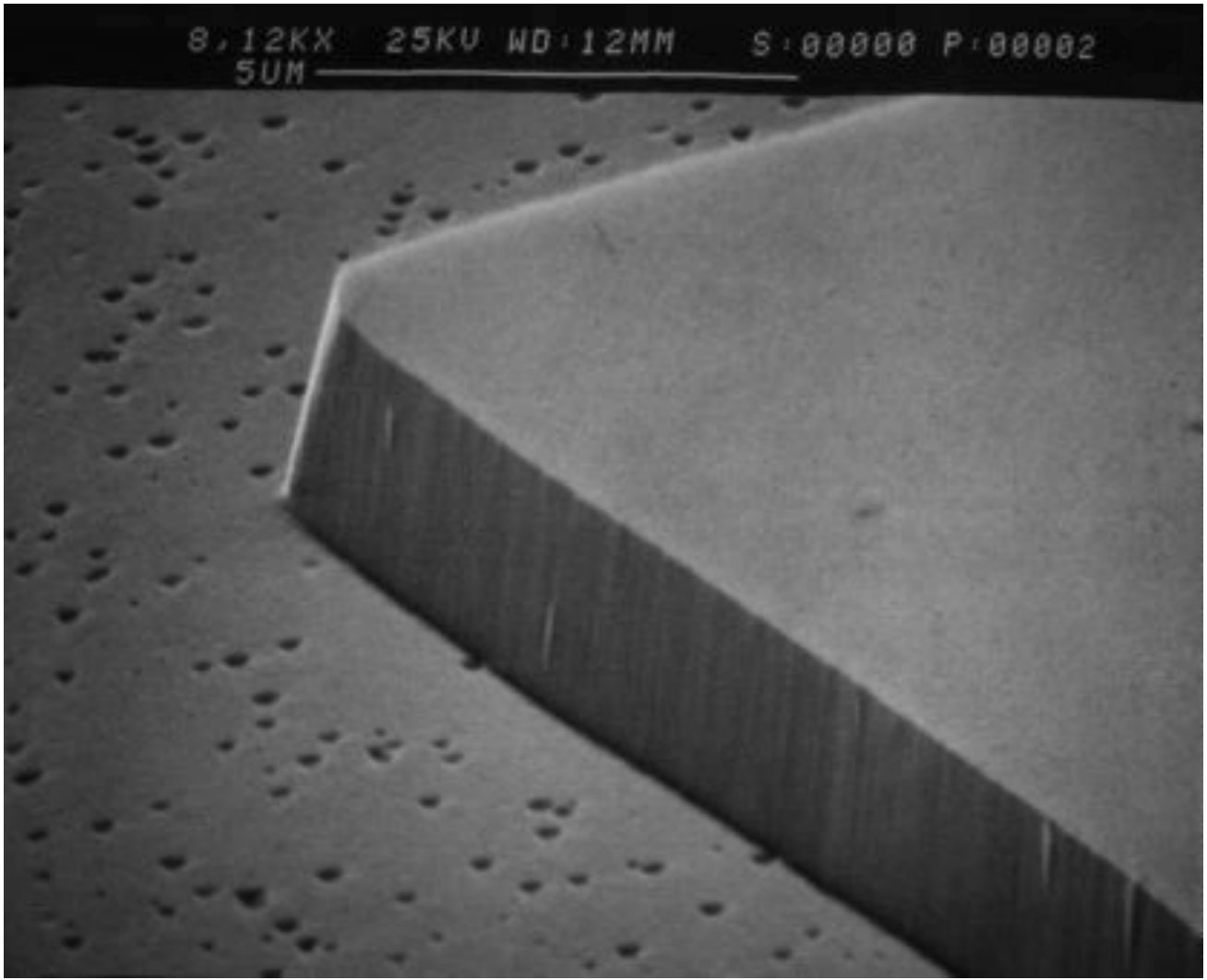**Figure 3**. Sample type 1 after etch
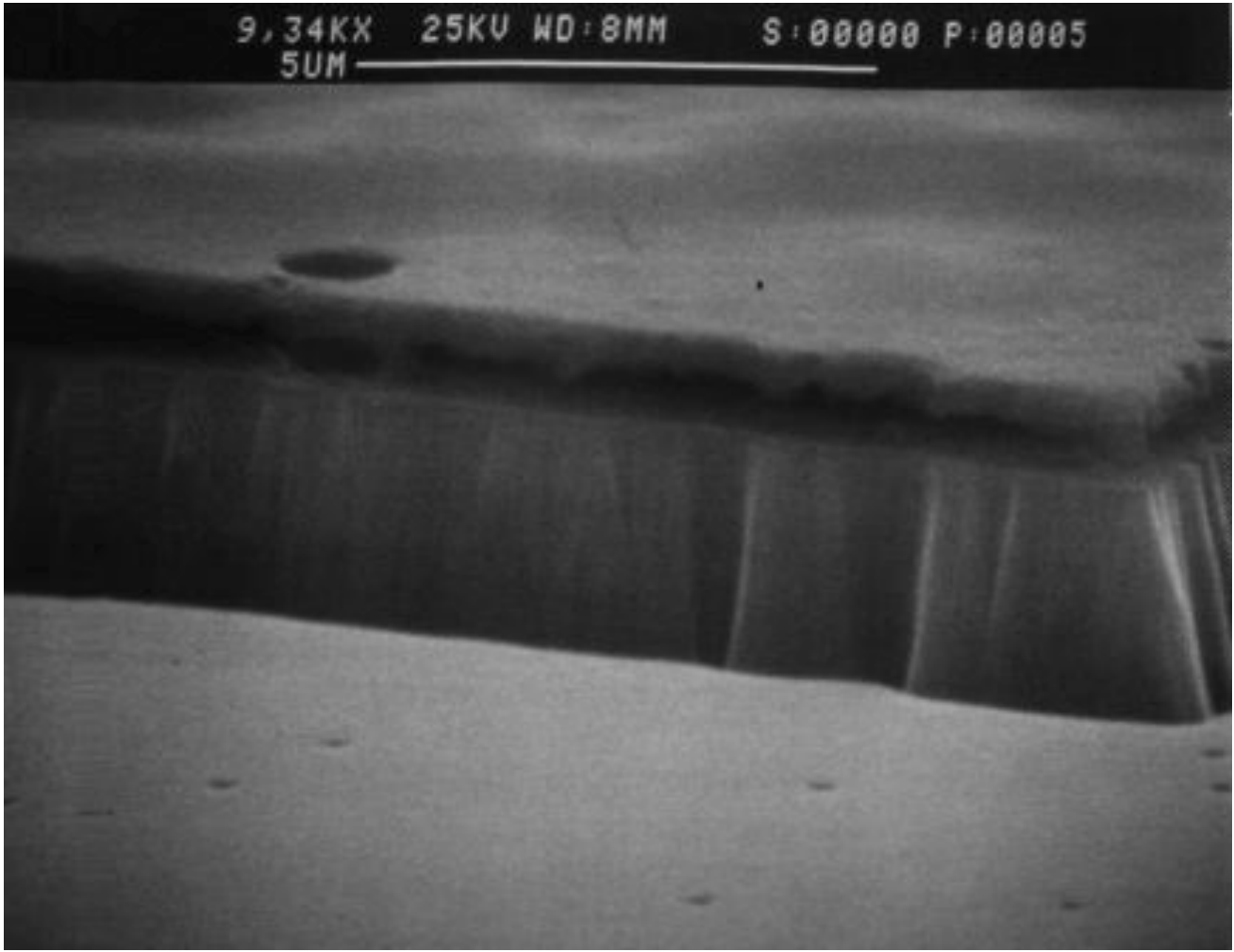
Figure 4. Sample type 1 after etch

Figure 5. Sample type 2 after etch
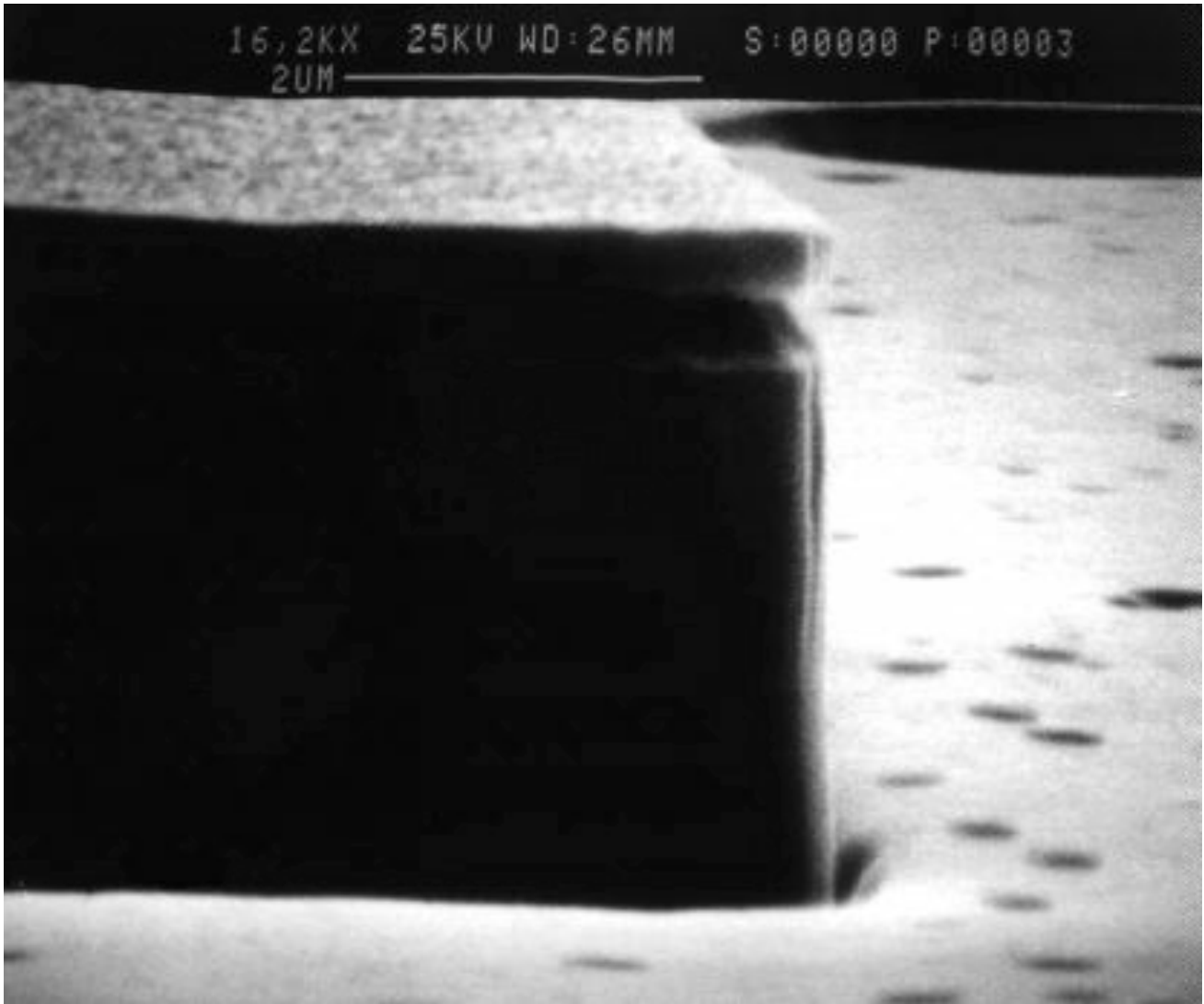
Figure 6. Sample type 2 after etch

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