Use of High Temperature Hydrogen Annealing to Remove Subsurface Damage in Bulk GaN

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Abstract

The results of a study to use atmospheric pressure annealing in hydrogen for etching GaN to remove damage from mechanical polishing is reported. Annealing in hydrogen ambient can achieve high removal rates. However, the highest removal rates at a given temperature result in an unacceptably rough surface morphology, possibly related to surface accumulation of Ga during the etching. Lower GaN removal rates maintained smooth surfaces for unpolished GaN. Faster etch rates are always observed for damaged material, with results suggesting that such differential etching may be suppressed at higher temperatures. Both photoluminescence and optical microscopy indicate mechanical polishing damage can extend as far as 2 μm into the sample, and could be removed by hydrogen annealing.

Introduction

The lack of a suitable lattice-matched substrate for the growth of GaN and related alloys remains a considerable impediment for low-cost commercialization of simple devices and for routinely achieving high performance devices and laser structures. Progress is being made, both in bulk growth of GaN and AlN as well as with thick, "free-standing" layers grown by hydride vapor phase epitaxy that were subsequently removed from substrates.[1] Both techniques lead to surfaces that must be polished, either to remove "saw" damage or to flatten the material for subsequent processing or epitaxial layer growth.[2] Removal of subsurface damage due to polishing has turned out to be a significant issue for wide band gap semiconductors such as SiC and GaN, as both are hard materials and are chemically inert.

This problem has been widely discussed concerning SiC, and indicates current chemo-mechanical polishing procedures practiced by commercial vendors leaves subsurface damage clearly deleterious to subsequent epitaxial layer growth or device fabrication. Recent studies have shown that annealing of SiC in a hydrogen ambient at or near atmospheric pressure leads to significant improvement in surface quality. H_2 annealing at temperatures of 1500 ^oC or greater leads to removal of damaged layers and/or surface recystallization, resulting in an atomically flat surface exhibiting atomic steps. [3,4]

Koleske et al.[5] have performed an extensive study of the decomposition of GaN in both nitrogen and hydrogen at pressures ranging from about 10 Torr to 760 Torr, although focusing on sub-atmospheric total pressures. Their work indicated that hydrogen could be used to significantly enhance decomposition of GaN for conditions pertinent to metal organic chemical vapor deposition (MOCVD) growth. While Ga-droplet formation was an issue, they indicated that, at least under some conditions, hydrogen-etched surfaces had large flat regions exhibiting

atomic steps. Based on this work, we decided to investigate whether annealing/etching in a hydrogen atmosphere could be used to remove subsurface damage in GaN related to mechanical or chemi-mechanical polishing. Our preliminary results are detailed in this paper.

Experimental Details

The samples used in this study were Ga-polar GaN layers grown on (0001) sapphire grown at TDI, Inc. using hydride vapor phase epitaxy (HVPE) with a nominal 13-μm thickness. One wafer was mechanically polished using a decreasing sequence of polishing grit, from 2 μm to 0.5 μm in order to produce a "damaged" surface. A second wafer was chosen due to its similar characteristics to serve as an "as-grown", unpolished comparison layer. The GaN layers were then sawn into 1cm by 1 cm squares. The samples were annealed in a tube furnace capable of attaining 1700^{o}C (CM Furnaces, Inc 1730-12 HT) although the highest temperature used in this study was 950^{o}C. The annealing ambient consisted of ultra high purity (6N) N_2, H_2 or a mixture of the two at a nominal flow rate of 2 liters per minute at atmospheric pressure through a 3.5 inch nominal diameter Al_2O_3 tube. Temperature ramp rates were limited to 200^{o}C per hour due to the thermal shock characteristics of the tube. A pure N_2 ambient was maintained until the anneal temperature was reached, and then the etching mixture was introduced. Samples were also cooled under pure N_2.

Mass loss was measured using a Mettler Toledo AX26 balance with a motorized glass draft shield, and fully automatic calibration using an internal weight. It was readable to $\pm$1 μgram, with a repeatability of 3 μgrams. This indicates that removal of less than 5 nm of GaN is, in principle, detectable with this instrument for 1-cm^2 sample sizes. Sample surface morphology was investigated using an Olympus BX60-M microscope in Reflected Light Nomarski

Differential Interference Contrast (DIC) observation mode. An additional green filter (550 nm) was used to further heighten the contrast of surface features. Both height and force images were obtained through Atomic Force Microscopy (AFM) measurements performed with a Digital Instruments Nanoscope II.

The photoluminescence (PL) measurements where performed at 6K with the samples placed in a continuous flown super varitemp cryostat. The 325 nm line of a HeCd laser was used to excite the samples. Combination of neutral density filters was employed to control the excitation density levels. The light emitted by the samples where collected with UV lenses and focused at the entrance slit of a 85 cm-double grating spectrometer fit with 1800 grooves/mm grating. The combination of an UV-sensitive GaAs photomultiplier and a computer controlled photon counter allowed the detection of low light levels.

Results

The first anneals performed were to evaluate GaN decomposition under pure N_2. No measurable weight loss was detected for anneal periods of up to 120 min at 850 ^{o}C, or at 900 ^{o}C for 90 min. This is in reasonable agreement with Koleske et al.'s results[5] for decomposition under N_2, which are shown in Figure 1 as curve (a). Our data point at 900 ^{o}C actually represents an upper limit on the etch rate. Comparison with the vacuum decomposition rates measured by Groh et al.[6] shown as the dashed line in Figure 1, curve (f), indicates that N_2 at atmospheric pressure suppresses thermal decomposition by two orders of magnitude. We note in passing that molecular beam epitaxy growth experiments at West Virginia University indicate vacuum decomposition rates in excellent agreement with Figure 1 (f) between 750 and 860 ^{o}C.

Several samples were then annealed for 60 min at 900 and 950 ^{o}C in a nominal 3:1 mixture of N_2 and H_2. Again, no mass removal was observed, indicating a very small decomposition rate. Koleske et al.[5] investigated the effect of the relative partial pressure of N_2 for sub-atmospheric pressure N_2:H_2 mixtures at 992 ^{o}C, and found that increasing the N_2 partial pressure lowers the decomposition rate dramatically. As outlined below, our results indicate this effect may be more drastic for atmospheric pressure mixtures with significant suppression of decomposition occurring for small partial pressures of N_2. No other mixing ratios were intentionally investigated.

Measurable GaN mass removal was only observed at these temperatures when using pure H_2. The resulting decomposition rates are summarized in Figure 1 and Table 1, with experimental details given in the table. The results obtained by Koleske et al.[5] for sub-atmospheric pressure decomposition of GaN in H_2 are also indicated in Figure 1 (curves b, c, d and e). Note that, as detailed in their paper, Koleske et al. found several distinct regimes to occur, indicating different dominant decomposition mechanisms for different pressures. Our result at 950 ^{o}C for a long (120 min) etch agrees well with both Koleske et al.'s higher-pressure results and Koukitu et al.'s[7] atmospheric pressure results for both polished and as-grown samples. A similar long etch at 900 ^{o}C led to a decomposition rate about a factor of two lower than Koleske et al. but again in reasonable agreement with Koukitu et al. for polished samples, but gave a significantly lower etch rate than either prior study for unpolished samples. As indicated in Table 1, higher etch rates were always observed for polished than for unpolished samples. Decomposition rates were enhanced by a factor of two to three at 900 ^{o}C for all conditions investigated, but only about 10% at 950 ^{o}C.

Of initial concern was the apparent decrease in decomposition observed with decreasing etch time. However, we now believe this decrease occurs for a rather prosaic reason – incomplete flushing of N_2 during the shorter anneals due to the relatively large tube volume and low flow rate coupled with non-optimal design of the reactor and gas distribution system. The several orders of magnitude decrease in decomposition for the 3:1 N_2:H_2 mixture indicates that even a small percentage of N_2 may significantly lower decomposition rates. This suggests that we did not achieve pure H_2 annealing conditions at least for the shorter etch times. Modified furnace design will be used on future work to minimize this effect.

Surface morphology for as-received and etched unpolished samples is shown in Figure 2 using optical DIC micrographs. As-received samples (Figure 2(a)) exhibited the textured surface morphology often seen with HVPE growth. The samples etched at less than 0.2 μm/hr exhibited an unchanged surface morphology except that subsurface damage possibly due to handling at the corners was revealed through differential etching. Figure 2(b) shows a "scratch" that was not observable prior to the annealing, located in a corner of the sample where tweezers were used to handle the sample. Several other scratches and other features were revealed during the slower etch, consistent with a faster etch rate for damaged material as discussed above. For etch rates above 0.4 μm/hr, the samples were extremely rough, including at 950 ^{o}C where differential etching may be lessened. This is illustrated by Figure 2(c) and 2(d). Whereas the samples shown in Figure 2(a) and 2(b) were "shiny" and exhibited specular reflection, those shown in 2(c) and 2(d) had a dull appearance reminiscent of a "ground glass" finish, underscoring the degree of surface roughness.

Figure 3 contains AFM images from these surfaces. The as-grown surface exhibited terrace-like features between 10 to 20 nm in height those were relatively flat on top. The overall surface

morphology exhibited "hillock" type features surrounded by the terraces (Figure 3(a)). The lower etch rate samples maintained these features away from revealed scratches, again with the flat terrace-like features (Figure 3(b)). We could not detect atomic steps on top of the terraces, but that was likely limited by the resolution of our AFM configuration. In contrast, the samples etched at the higher rates all exhibited extremely rough surfaces with tall, sharp features as indicated in Figure 3(c) where we only saw repeated traces of the AFM tip itself, indicative of features with a large height to width ratio, with the actual feature width significantly smaller than the approximately 500 nm dimension of the pattern observed.

Figure 4 contains DIC micrographs of polished surfaces etched under similar conditions to Figure 2. Polishing scratches were very evident in the un-etched and lightly etched samples, as shown in Figure 4(a) and 4(b). The scratch damage seemed to be removed in one sample after ~2 μm of GaN was removed, but was still apparent in a second sample undergoing the same annealing conditions and GaN removal. This suggests that the polishing damage extends ~2 μm into the GaN, and is also non-uniform in depth across the wafer. AFM investigation of these surfaces did not reveal any additional information than that contained in Figure 4.

Photoluminescence was used to investigate damage removal in the layers, and to verify the possibility of significant changes in defect content. Figure 5(a) shows the near edge PL of an unpolished sample before and after H_2 annealing at 900 ^oC for 30 min, resulting in the removal of 0.08 μm. Both PL spectra are dominated by recombination process involving excitons bound to a neutral donor impurity or impurities [8]. Other than a slight peak shift and a slight broadening, which may be associated with sample inhomogeneities, there were no significant changes in the PL spectrum. This is in sharp contrast to the result obtained for polished samples. Figure 5(b) shows the same spectral region before and after etching of 2 μm of material from a polished

sample. Although PL is not a quantitative technique due to competition between different recombination channels, the observed dramatic increase of the near-bandedge PL peak intensity indicates that significant damage removal is occurring. Figure 5(c) represents the below-edge PL observed for the same sample as shown in Figure 5(b). Although etching under these conditions apparently produces quite a rough surface, the etching itself does not appear to introduce new features in the spectral regions investigated. Figure 6 illustrates the evolution of the increasing near-bandedge PL peak intensity with increasing etch depth. A plateau is reached after the removal of 2 μm of material.

Discussion

H_2 enhances decomposition of GaN at atmospheric pressure. It appears that H_2 etching is differential, etching two to three times faster in damaged regions at 900 ^oC with limited data suggesting the effect is lessened at the higher temperature of 950 ^oC. This result suggests that lower temperature H_2 annealing could be used to reveal subsurface damage. The appearance of scratch remnants apparently due to handling indicates that introduction of subsurface damage into GaN may be easier than commonly believed based on its relative hardness. The apparent suppression of differential etching at higher temperature may simply reflect that the etch rate for both damaged and undamaged material is fast enough to be limited by either Ga desorption or the transport of H_2 through a surface "boundary" layer. The actual mechanism cannot be determined from the limited data. Both the etching studies and PL characterization indicate the mechanical polishing damage can extend fairly deep into the sample, of order 2 μm for the polishing conditions used here.

The extreme surface roughness observed for most of our annealing conditions is a significant concern for using H_2 etching as part of a process for producing damage-free surfaces. The origin of the roughness may be due to the fact that it is possible to cause GaN decomposition at a rate faster than Ga removal, resulting in significant surface accumulation of Ga. Indeed, Ga-droplet formation has been observed in other studies,[2,5,7] and the reason we did not see Ga coverage is that the Ga likely desorbs during our cool-down cycle. Figure 7 indicates Ga desorption rates determined by Koleske et al. under either N_2 or H_2 at sub-atmospheric pressure. It can be seen that Ga desorption is also enhanced by H_2. Also included are the decomposition rates we measured. All of the rough samples are near or above the H_2 Ga-desorption rate limit, strongly suggesting that Ga accumulation is occurring and may play a strong role in the origin of the roughness. Smooth surfaces for unpolished samples were only maintained for lower etch rates, suggesting that regimes exist for enhanced etching (above the rates for a pure N_2 ambient) that does not exceed the Ga-desorption rate. However, the differential etching observed at the temperatures investigated would still cause problems. The next step will be to repeat some of these experiments in an improved set-up allowing complete purging of gas going into the etch cycle, and to investigate whether increasing the annealing temperature while maintaining the correct Ga-desorption conditions can lead to conditions allowing both damage removal and the creation of high quality surfaces.

Conclusions

The use of atmospheric hydrogen annealing can achieve significant etch rates in GaN through enhanced decomposition. However, the Ga desorption rate is not increased by the same factor, suggesting that surface accumulation of Ga may interfere with the etching thereby creating the rough surface morphology observed for the highest GaN removal rates in this study.

Both PL and optical DIC microscopy indicate that hydrogen etching can remove subsurface damage due to mechanical polishing. Limited results suggest that a mixture of hydrogen and nitrogen may be used to achieve reasonable etch rates while allowing adequate Ga-desorption to occur. Preliminary results suggest the use of temperatures greater than 950 ^{o}C may suppress differential etching effects.

Acknowledgements

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Table 1. Summary of H_2 etching experiments.

Sample Type	Anneal Time	Etch "Depth"	Rate	Ratio
(Anneal Temperature)	minute	μm	μm/hr	Polished /unpolished
950 °C				
polished	120	9.6	4.8	
unpolished		9.1	4.5	1.1
polished	15	0.53	2.1	
unpolished		0.48	1.9	1.1
900 °C				
polished	15	0.11	0.43	
unpolished		0.04	0.18	2.4
polished	30	0.26	0.51	
unpolished		0.08	0.17	3.1
polished	60	2.0	2.0	
polished		2.0	2.0	
unpolished		0.78	0.78	2.6

Figure Captions.

Figure 1. GaN decomposition under various experimental conditions. The details of curves (a), nitrogen ambient, and (b), (c), (d), and (e), hydrogen ambient, are detailed in reference 5. The vacuum decomposition curve, (f), is taken from reference 6. The discrete points are results from this study.

Figure 2. Optical DIC micrographs of (a) an as-received surface; (b) lightly-etched surface revealing scratch damage due to differential etching; (c) and (d) rough surface morphology for higher etch rates. All samples were etched at 900^{o}C, except (d).

Figure 3. AFM micrograph of (a) an as-received, unpolished surface (70 nm in z); (b) shallow-etched (0.08 μm removed) unpolished surface (50 nm in z) and (c) an etched (2.0 μm removed) polished surface (by 200 nm in z). All samples were etched at 900^{o}C.

Figure 4. Optical DIC micrographs of (a) an as-polished surface; (b) shallow-etched surface; and (c) and (d) rough surface morphology for deeper etching. Note that evidence of scratches have been removed in (c) but remain evident in (d). All samples were etched at 900^{o}C.

Figure 5. Comparison of near-bandedge PL spectrum before and after etching of an (a) unpolished (0.08 μm removed) and (b) polished sample (2.0 μm removed). Plot (c) compares lower energy PL spectrum for the samples shown in (b).

Figure 6. Evolution of near-bandedge PL intensity for polished samples with varying amounts of GaN removed.

Figure 7. Comparison of decomposition rates to Ga desorption rates taken from reference 5.

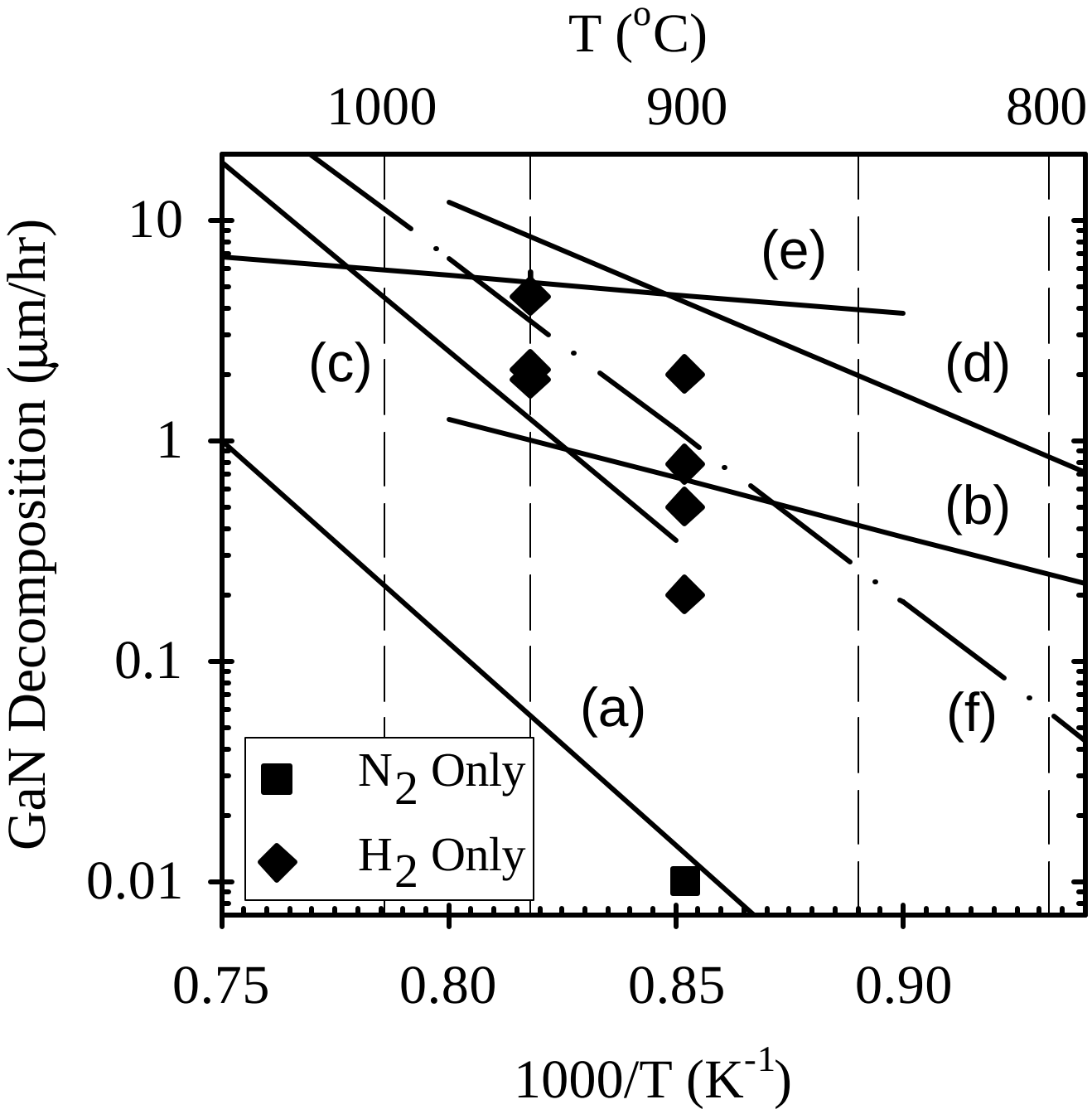
T (°C)
1000
900
800
GaN Decomposition (μm/hr)
10
1
0.1
0.01
(a)
(b)
(c)
(d)
(e)
(f)
N2 Only
H2 Only
0.75
0.80
0.85
0.90
1000/T (K-1)

Figure 1

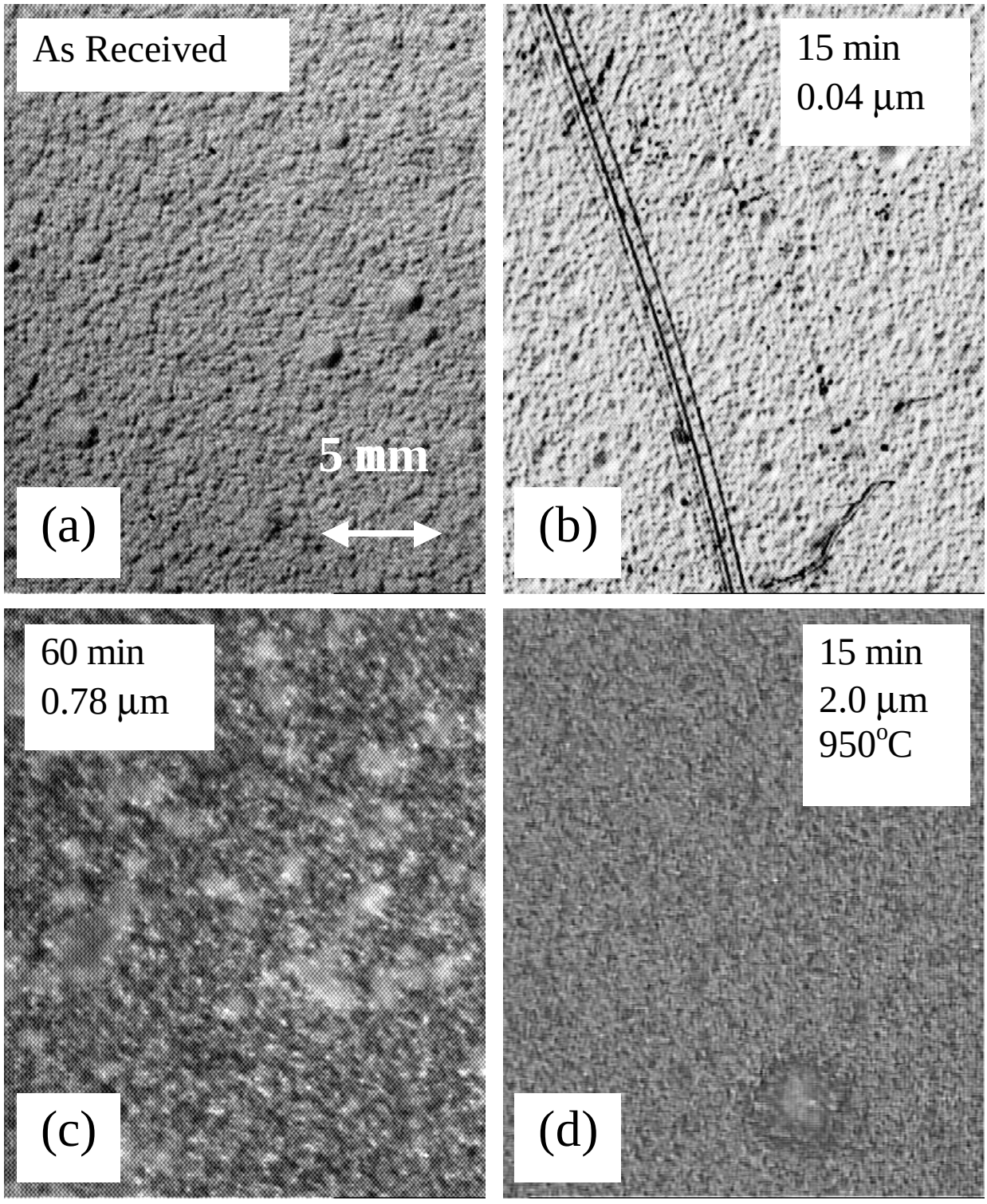
As Received
5 mm
(a)
15 min
0.04 μm
(b)
60 min
0.78 μm
(c)
15 min
2.0 μm
950°C
(d)

Figure 2

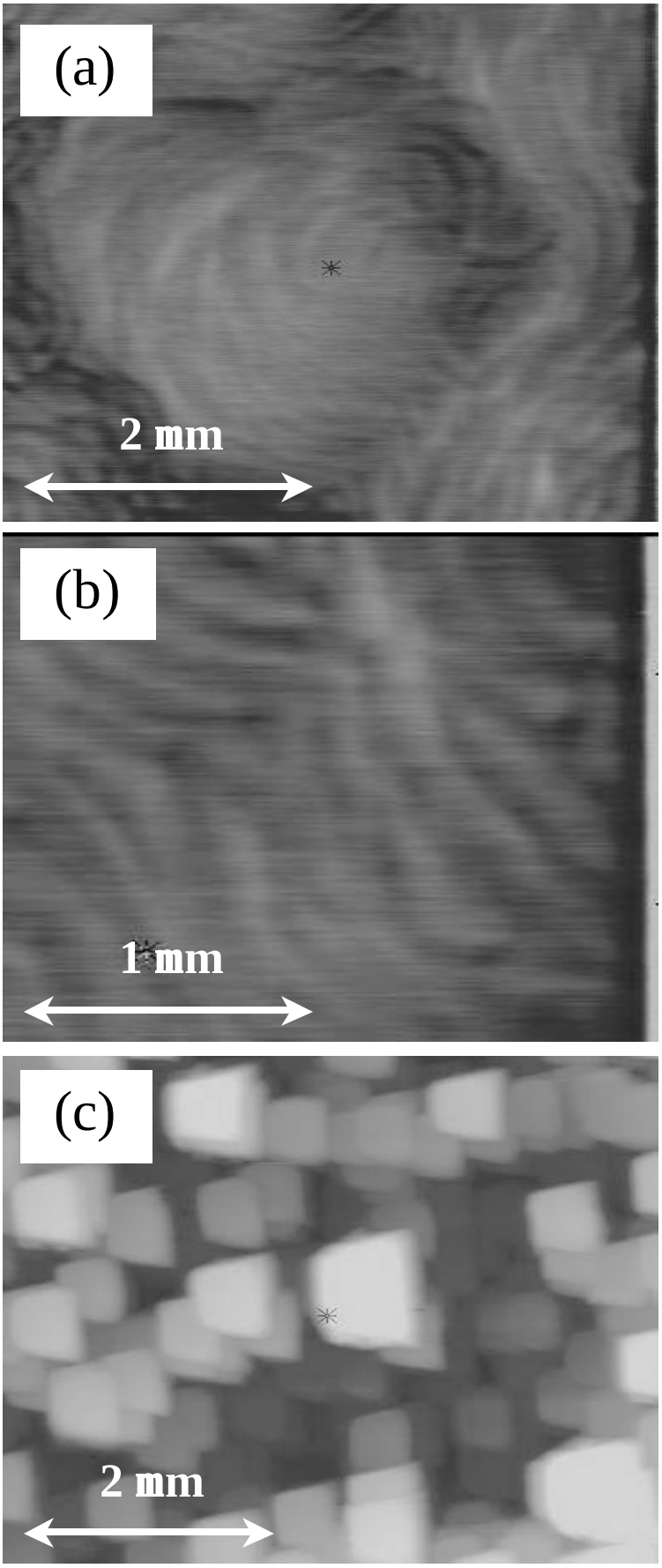

Figure 3

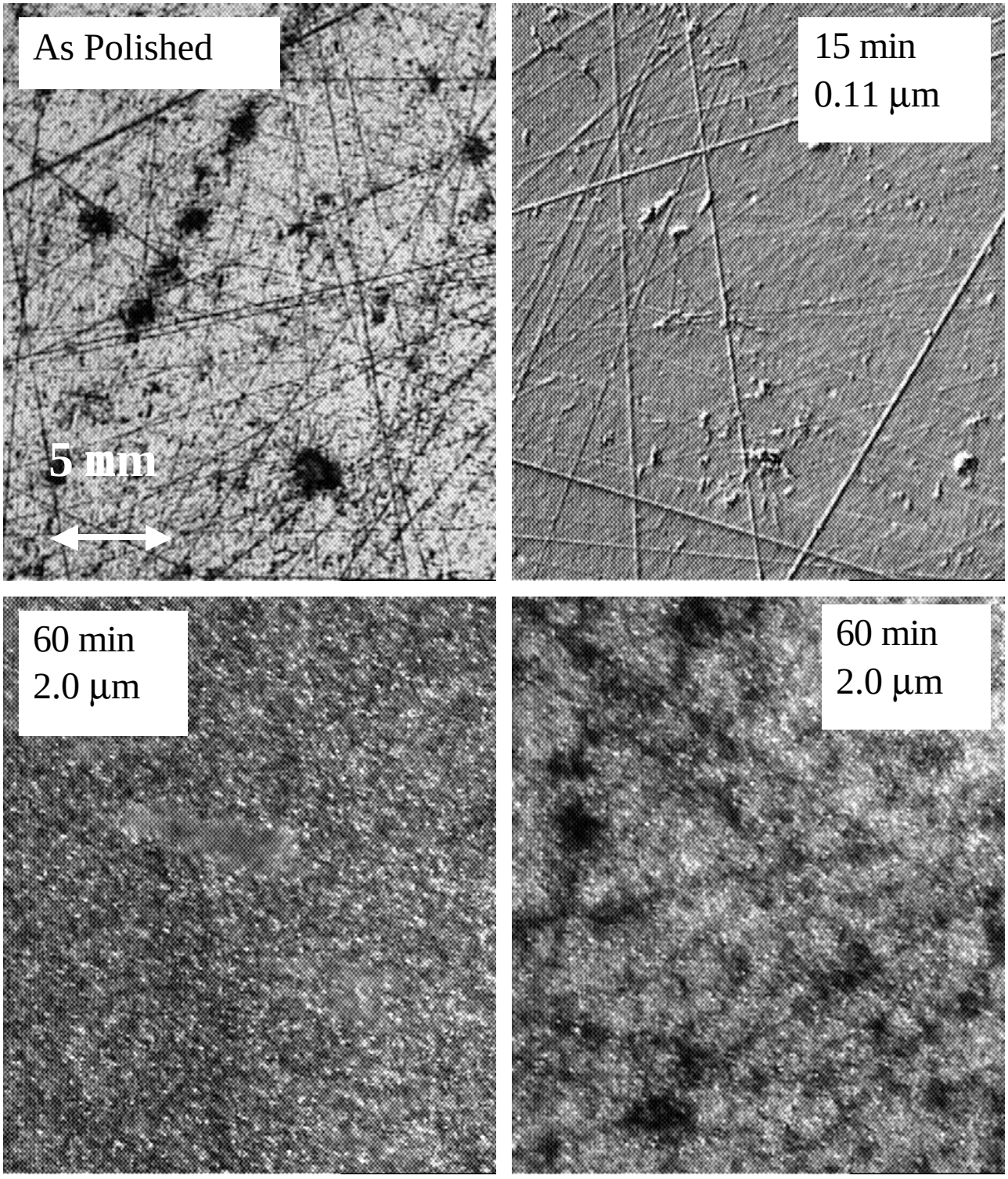

Figure 4

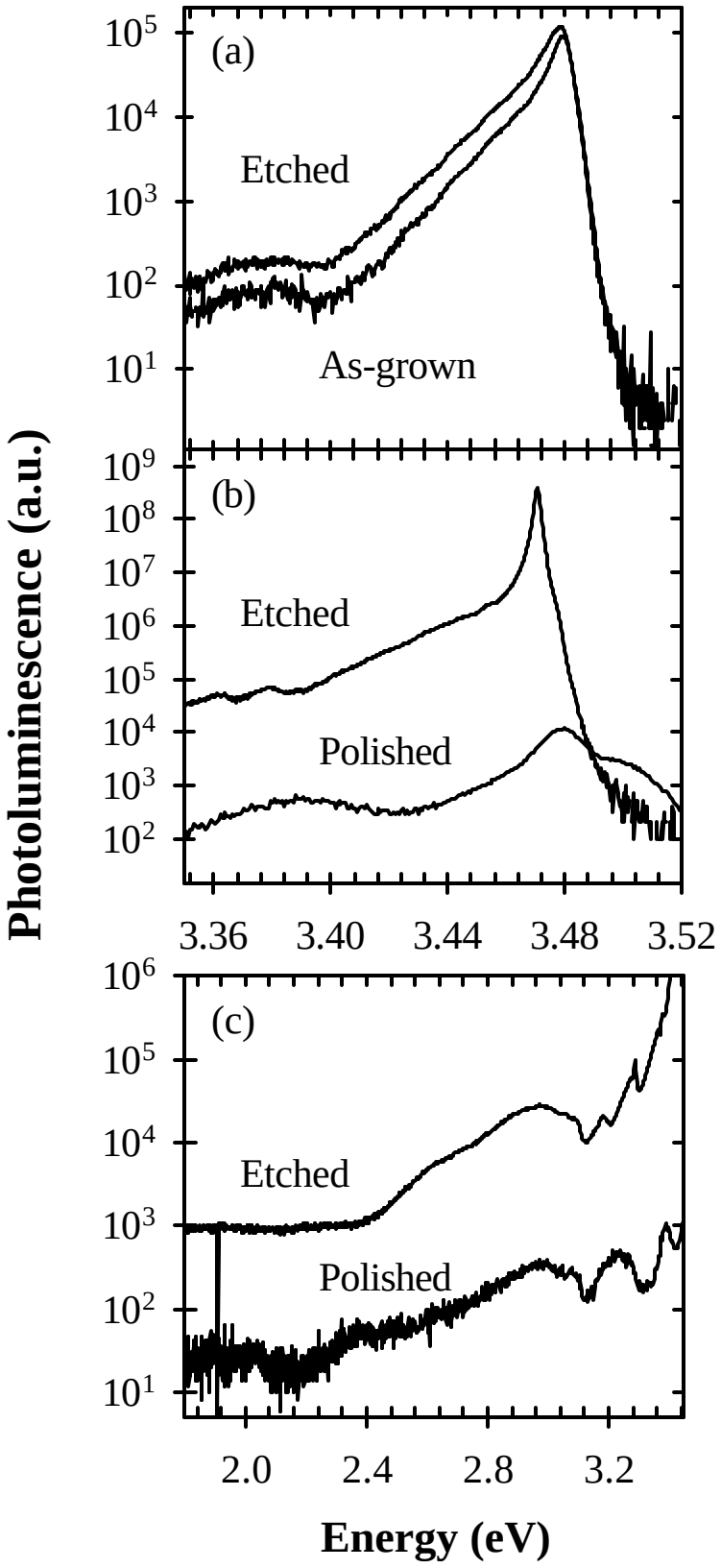
(a)
Etched
As-grown
(b)
Etched
Polished
(c)
Etched
Polished
Photoluminescence (a.u.)
Energy (eV)
3.36
3.40
3.44
3.48
3.52
2.0
2.4
2.8
3.2

Figure 5

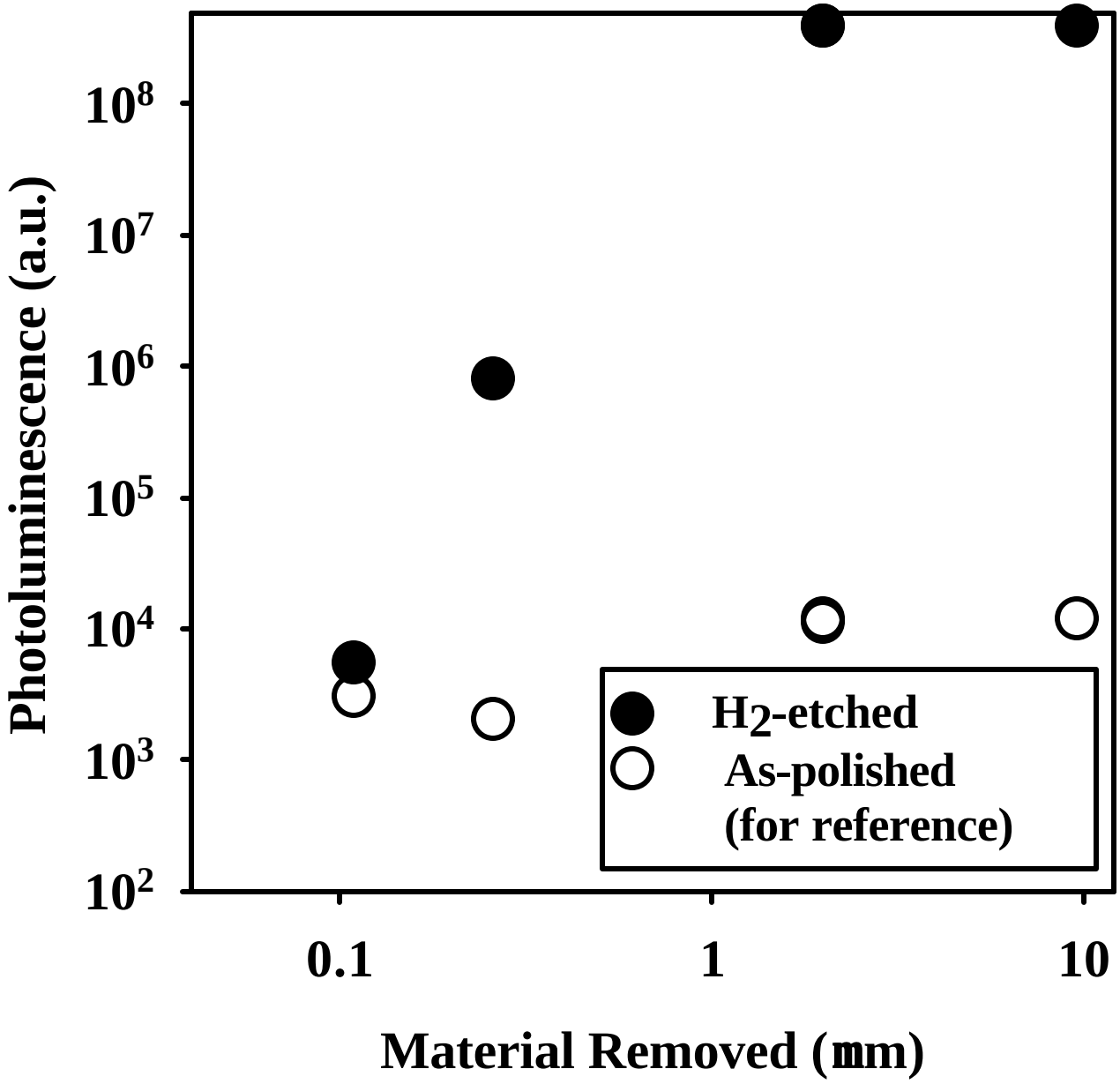
Photoluminescence (a.u.)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
0.1
1
10
Material Removed (mm)
H2-etched
As-polished
(for reference)

Figure 6

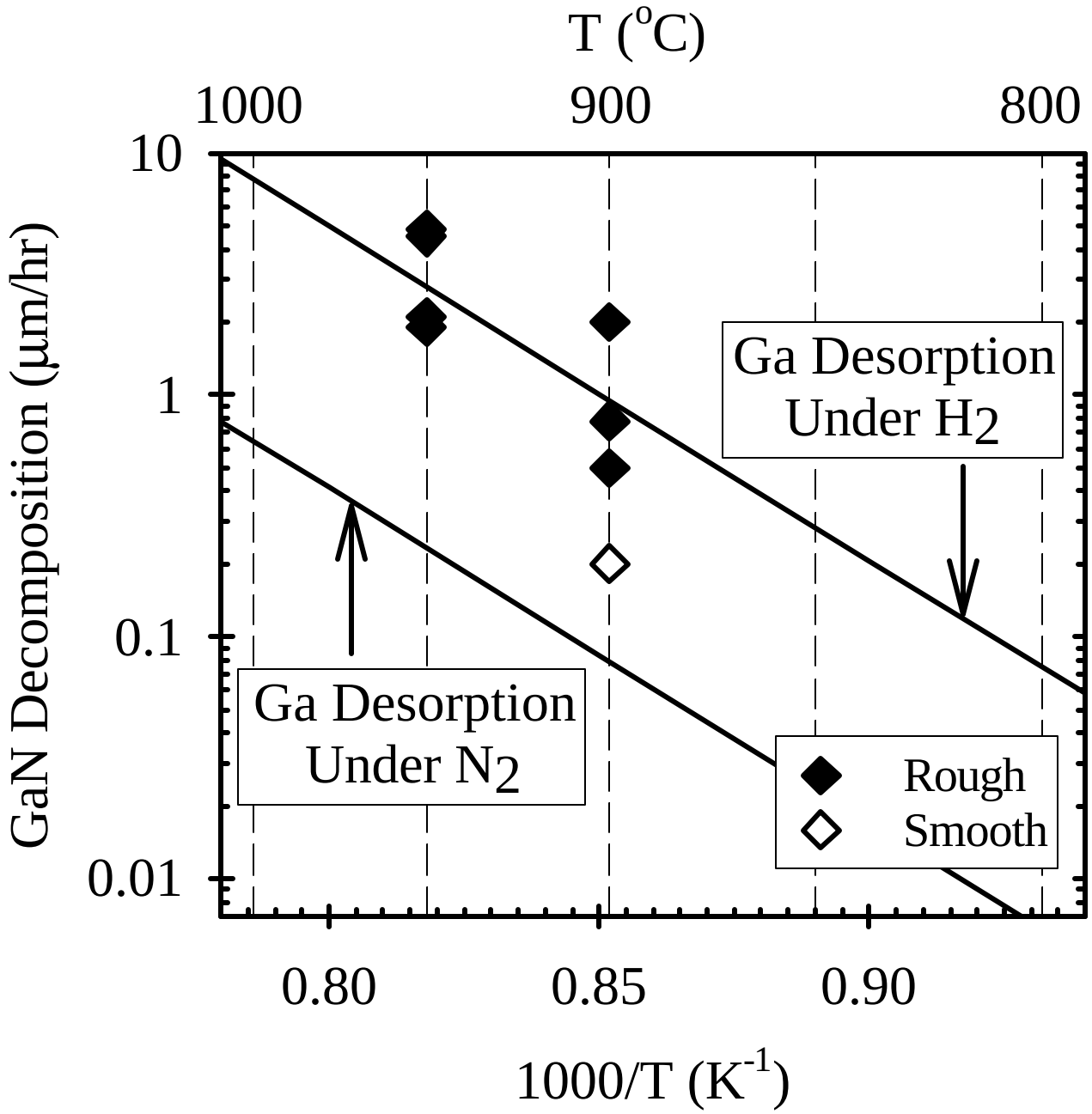
T (°C)
1000
900
800
10
1
0.1
0.01
GaN Decomposition (μm/hr)
Ga Desorption
Under H2
Ga Desorption
Under N2
Rough
Smooth
0.80
0.85
0.90
1000/T (K-1)

Figure 7