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Fundamental Investigation of Chemical Mechanical Polishing of GaAs in Silica Dispersions: Material Removal and Arsenic Trihydride Formation Pathways

J. B. Matovu,[a,b] P. Ong,[b] L. H. A. Leunissen,[b] Sitaraman Krishnan,[a] and S. V. Babu[a,*,z]

[a]*Department of Chemical and Biomolecular Engineering and Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699, USA*
[b]*IMEC, 3001 Heverlee, Belgium*

The fabrication of InGaAs *n*-channels in CMOS devices requires an intervening buffer layer of GaAs or InP between a Si substrate and the InGaAs channel layer, which has to be planarized to enable the growth of a channel that is free of defects due to uneven surface topography. This report discusses the material removal rates (RRs) and AsH_3 evolution observed during chemical mechanical polishing (CMP) of GaAs using aq. solutions of hydrogen peroxide (H_2O_2) and silica slurries containing H_2O_2. GaAs RRs were negligible with deionized water or with silica slurries alone. They were relatively high in aq. solutions of H_2O_2 alone and showed a strong pH-dependence, with significantly higher RRs in the alkaline region. The addition of silica particles to aq. H_2O_2 did not increase the GaAs RRs significantly. The evolution of arsenic trihydride (AsH_3) during the dissolution of GaAs in aq. H_2O_2 solution was similarly higher in the basic pH range than in neutral pH or in the acidic pH range. However, no AsH_3 was measured during polishing, evidently because of the relatively high water solubility of AsH_3. In this report, GaAs removal rates and AsH_3 formation are analyzed using data from contact angle measurements, X-Ray photoelectron spectroscopy (XPS), and X-Ray fluorescence (XRF) spectroscopy. Reaction pathways leading to material removal are proposed.
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The quest for faster devices in the microelectronic industry has renewed interest in III-V materials such as InP, GaAs, and InGaAs as *n*-channel candidates because of their high electron mobility.[1,2] During the fabrication of *n*-channels in CMOS devices, chemical mechanical polishing (CMP) of these materials is required to achieve a smooth and planar surface to enable further processing. There are several environmental health and safety (EHS) issues associated with polishing and wet processing of these III-V materials.[2–5] The EHS concerns for As containing materials include the evolution of toxic arsenic trihydride (AsH_3) gas, and the handling of arsenic contaminated slurry waste and used consumables (e.g., polishing pads). For InP, the major concern has been the generation of toxic phosphine gas during polishing.[3,4] In this work, the focus is on the chemical mechanical polishing of GaAs and evolution of AsH_3.

There are several reports on the CMP of GaAs using slurries that contain oxidizers such as hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), and dibromine (Br_2).[6–9] McGhee et al.[6] proposed a three step mechanism for GaAs removal in an aqueous solution containing H_2O_2 and ammonia. An oxohydroxyl layer, consisting of sparingly soluble oxohydroxides of Ga and As, was first formed on the surface. These oxohydroxides were converted to soluble species upon complexation with aq. NH_3. The soluble species were then removed from the surface by mechanical wiping. In Br_2-MeOH solutions, they proposed that an adsorbed Br layer was formed on the GaAs surface. The adsorption of bromine was followed by a redox reaction, which continued as long as Br_2 was present. $GaBr_3$ and $AsBr_3$ were formed, which were subsequently converted to oxohydroxides (by methanolysis) that were soluble in MeOH. Because of the uncontrolled reaction with Br_2, the surface finish of GaAs obtained after polishing with Br_2-MeOH was found to be poor.[6] Furthermore, the use of Br_2 oxidant is undesirable in CMP due to the presence of toxic bromine vapors.[10] Hydrogen peroxide has been preferred because it leads to smoother polished GaAs surfaces as well as good material removal rates.[6,9]

In this work, we investigated GaAs removal rates in the presence of H_2O_2 and silica particles and compared them with those obtained in the presence of other oxidizers such as sodium iodate and sodium periodate. The pH of the aqueous phase of the slurry and the type of oxidizer were both found to have a strong effect on material removal rates (RRs). Using calculated standard Gibbs free energy values of the reactions possible during CMP of GaAs surfaces, along with results from X-ray photoelectron Spectroscopy (XPS) and contact angle measurements on the polished surfaces, this report discusses the observed trends in material RRs and AsH_3 formation and identifies process conditions that lower AsH_3 formation.

Experimental

Chemical mechanical polishing.— Blanket GaAs coupons (2.6 × 2.9 cm^2), diced from a 4″ GaAs wafer of approximately 450 μm thickness and supplied by IMEC, were polished on an Alpsitec E460 Mecapol Polisher. Nexsil 35A (Nyacol Nanotechnologies, Inc.), a 30 wt% aqueous dispersion of colloidal silica particles with a mean particle size of approximately 35 nm, was used as the abrasive. Hydrogen peroxide oxidizer (30 wt% in water, unstabilized) was obtained from Ashland Chemical Co. Other oxidizers such as sodium iodate ($NaIO_3$, CAS no. 7681–55-2, ≥99% purity) and sodium periodate ($NaIO_4$, CAS no. 7790–28-5, ACS reagent, ≥99.8%) obtained from Sigma Aldrich were used without purification.

As an example, a polishing slurry was prepared by mixing 100 g of Nexsil 35A colloidal silica dispersion, 33.33 g of H_2O_2 solution and 866.67 g of deionized (DI) water using a magnetic stirrer for about 5 min to yield a slurry with 3 wt% silica particles and 0.3 mol dm^{-3} (∼1 wt% of the slurry) H_2O_2. The number concentration of silica particles in the slurry, calculated using their mass concentration (3 wt%), the mean particle diameter (≅35 nm), and particle density (≅2.2g/cm^3) was about 6.26×10^{17} particles/dm^3. The pH of the slurry thus prepared was adjusted using nitric acid or potassium hydroxide, and the slurry was used immediately for CMP experiments to minimize loss of oxidation ability because of decomposition.[6]

The polishing conditions used were: carrier/platen rotation speed of 80/72 rpm, slurry flow rate of 200 mL min^{-1}, polishing time of 1 min and operating pressure of approximately 24 kPa (3.5 psi). All the polishing experiments were performed using an IC1000 K-groove pad. The pad was conditioned using a diamond grit conditioner for 30 s before each experiment.

The removal rates, averaged over 3 experiments, were determined from the change in mass obtained using a Metryx Mentor balance with a precision of 1.0 μg, before and after polishing the coupons. The coupons were dried in a stream of nitrogen gas after polishing. A density of 5.32 g cm^{-3},[11] corresponding to that of GaAs, was used to convert the mass loss rates into material thickness reduction rates.

*Electrochemical Society Active Member.
zE-mail: babu@clarkson.edu

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GaAs dissolution experiments.— Dissolution experiment was performed using 200 mL of the test solution and a 1.8×1.8 cm^2 GaAs blanket coupon (diced form a 4″ GaAs wafer of approximately 450 μm thickness), placed in a 2000-mL conical flask fitted with a side arm for collecting gases that were released during dissolution. The solution in the flask was maintained at a temperature of 40°C using a hot plate, to better mimic the actual temperature during CMP,[12] and was stirred using a magnetic stirrer to reduce mass transfer limitations for material removal from the surface into the solution. Before the dissolution experiment, the GaAs coupon was dipped in a 2 M aq. HCl cleaning solution to remove any surface contaminants, dried in a nitrogen stream, and weighed using a Sartorius analytical balance with an accuracy of 0.1 mg. It was, thereafter, immersed in the test solution for 30 min. The relatively long dissolution time was used for better reliability of measurements when the dissolution rate was low. The coupon was removed from the test solution, dried using a stream of nitrogen gas, and weighed. The difference in the masses of the coupon before and after immersion in the test solution was used to calculate the dissolution rate. The reported values are averages from three replicate analyzes.

AsH_3 concentration measurement.— The concentration of AsH_3 evolved during polishing and dissolution was measured for each experiment using an MDA Scientific CM4 Four point Continuous Gas Monitor from Honeywell. During polishing, the AsH_3 concentration was measured by placing a gas collection tube at a location that was approximately 3 cm above the pad and 5 cm from the center of the wafer, and connecting the other end of the tube to one of the four ports of the detector. The flow system of the instrument included a pump that sampled gas at a constant rate of 720 cm^3 min^{-1} at standard ambient temperature and pressure (SATP). $AsH_3(g)$ concentration was determined using the Chemcassette detection system, which optically measured the density of the stain developed by the gas on a reactive Chemcassette tape. The concentration of the gas, which is proportional to the stain density, was recorded in parts-per-billion (ppb).

The amount of AsH_3 released during the dissolution experiments (conducted at 40°C) was measured by connecting a gas collection tube of one of the four ports of the detector to the side arm of the conical flask (containing the GaAs coupon and 200 mL of the test solution) through a cold trap maintained at 20°C for dehumidification. A record of the concentration, y, of AsH_3 in air (v/v) as function of time, t, was made for each of the dissolution experiments. The mass of AsH_3 formed was estimated based on the instantaneous concentration of AsH_3 detected in the gas flowing through the detector, the volumetric flow rate, Q, of the gas (720 cm^3 min^{-1} at SATP), and the density, ρ, of AsH_3 gas [3.42×10^{-3} g cm^{-3} at SATP,[11]] The product, $y \times Q \times \rho$, is the instantaneous mass generation rate of $AsH_3(g)$ and its integration with respect to time t, over the entire duration of the dissolution experiment (30 min) gave the total mass of AsH_3 evolved.

Surface roughness measurement.— The as-received and polished GaAs coupons were characterized using the Digitial Instruments Nanoscope IVa Dimension 3100 Atomic Force Microscope in the tapping mode. Root-mean-square (RMS) surface roughness values were determined from 2×2 μm^2 scans.

Surface wettability.— Water drop contact angles were measured using a Dataphysics OCAH230L contact angle goniometer. The contours of a water droplet on the coupon were recorded by means of a CCD camera and the contact angle was estimated using drop shape analysis. The contact angles were measured on square (1.8×1.8 cm^2) GaAs blanket coupons (same as in section 2.2) after dipping in solutions containing H_2O_2 at pH 2 or 10 for 1 min, rinsing in DI water for 10 s, and drying in a nitrogen stream. The contact angles for coupons dipped in H_2O alone were also determined for comparison. The uncertainty in the reported values of contact angles is about 2 degrees.

X-Ray photoelectron spectroscopy (XPS).— Surfaces of GaAs blanket coupons, (1.8×1.8 cm^2) dipped for 1 min in pH-adjusted aqueous solutions of H_2O_2 (0.3 M), were analyzed by XPS. Two different samples prepared using aq. H_2O_2 solutions of pH 2 and pH 10, respectively, were studied. The surfaces were dipped in DI water for 10 s and dried using a stream of nitrogen gas before XPS measurements. A GaAs coupon dipped in DI water alone, and another coupon dipped in 3 mM aq. $NaIO_4$ solution (at pH 2), were used as references. XPS measurements were carried out in angle resolved mode, with electron emission angles in the range of 22 to 78°, using a Theta300 spectrometer from ThermoInstruments. Spectra were acquired using a monochromatized Al Kα X-ray source (1486.6 eV) and a spot size of 400 μm. The spectra reported herein were acquired at an emission angle of 56°. The probe depth corresponding to this angle of measurement is approximately equal to $\lambda \cos 56°$, where λ is the mean free path of electrons in GaAs, estimated to be about 2.19 and 2.16 nm, respectively, for the Ga 3d and As 3d photoelectrons emitted from our samples.[13] Thus, approximately the top 1.2 nm was probed at this emission angle.

X-Ray fluorescence (XRF) study of post-polishing slurry.— XRF experiments were conducted to estimate the concentration of As and Ga in the post-CMP slurry. The aq. slurries (200 mL) which were used for polishing GaAs surfaces (2.6×2.9 cm^2) were collected along with the post-polishing cleaning water (100 mL). A slurry thus collected was centrifuged to separate the solids from the liquid, and both the solid and liquid phases were analyzed. About 5 g of the solid phase and 10 g of the liquid phase were dried completely at 50°C and used for XRF elemental analysis. The XRF analysis was performed using an X-Lab 2000 energy dispersive X-ray fluorescence spectrometer. Slurries collected from two different polishing experiments, at pH 2 and pH 10, were characterized. The uncertainty in the calculated mass of Ga or As is estimated to be less than 20% of the reported value.

Results and Discussion

Thermodynamic analysis of reactions involved during chemical dissolution and chemical mechanical polishing of GaAs.— Table I lists the potential chemical reactions involved in the dissolution of GaAs, along with the standard Gibbs energy of reaction, $\Delta_{rxn}G°$, calculated using the Gibbs free energy of formation and the standard electrochemical potentials available in the literature.[11,14] $\Delta_{rxn}G°$ is the Gibbs free energy of reaction at 298.15 K (25°C), a pressure of 101.3 kPa (1 atm), and at concentrations of reactants and products at which their activities are equal to 1. Although these conditions of temperature, pressure, and concentrations are different from those of the polishing and dissolution experiments, a comparison of the values of the Gibbs free energy of reaction, at the standard state, provides a quantitative insight into the chemical effects of pH and oxidizer on GaAs.

The surface film of GaAs under ambient conditions consists of gallium oxides and arsenic oxides,[15] whose formation is thermodynamically favored (cf. $\Delta_{rxn}G°$ for reaction 1). Previous studies[15,16] have discussed the instability of As_2O_3 in the presence of GaAs, leading to the formation of As, as depicted by reaction 2. The insoluble Ga_2O_3 could act as a passivating layer, preventing dissolution of GaAs, but can be removed by reactions in strongly acidic or basic media to form soluble gallium salts [see reactions 4 to 6, which show the formation of Ga^{3+} and $Ga(OH)_4{}^-$, in acidic and basic pH, respectively[17]]. Other soluble species such as $Ga(OH)^{2+}(aq)$, GaO^+, $GaO_2^-(aq)$, $HGaO_3^{2-}(aq)$, $H_2GaO_3^-(aq)$ and $GaO_3^{3-}(aq)$ have also been postulated.[15,18] However, the reactions leading to their formation are not shown in Table I. The passivating layer of Ga_2O_3 is stable over a pH range of approximately 3 to 11,[16,19] and the dissolution of GaAs is expected to be low over this pH range. As_2O_3, on the other hand, is soluble over a wide range of pH because of reactions such as 7 and 8 that lead to the formation of soluble arsenic compounds, such as arsenenous acid (O=As–OH, CAS no. 13768-07-5), arsenous acid ($As(OH)_3$, CAS no. 13464-58-

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Table I. Standard state Gibbs free energy of reaction, $\Delta_{rxn}G^\circ$ (kJ mol^{-1}), at unit activities of reactants and products. The physical states of the reactants and products are indicated by *s* for solid, *l* for liquid, *aq* for aqueous (dissolved species), and *g* for gas.

#	Reaction	$\Delta_{rxn}G^\circ$
1	$GaAs(s) + \frac{3}{2}O_2(g) \rightarrow \frac{1}{2}Ga_2O_3(s) + \frac{1}{2}As_2O_3(s)$	–719.1
2	$GaAs(s) + \frac{1}{2}As_2O_3(s) \rightarrow \frac{1}{2}Ga_2O_3(s) + 2As(s)$	–143.6
3	$Ga_2O_3(s) + 6H^+(aq) \rightarrow 2Ga^{3+}(aq) + 3H_2O(l)$	–31.2
4	$Ga_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Ga(OH)_4^-(aq)$	– 18.2
5	$GaAs(s) + 3H^+(aq) \rightarrow Ga^{3+}(aq) + AsH_3(g)$	–22.3
6	$GaAs(s) + 3H_2O(l) + OH^-(aq) \rightarrow Ga(OH)_4^-(aq) + AsH_3(g)$	– 15.8
7	$As_2O_3(s) + 3H_2O(l) + O_2(g) \rightarrow 2H_3AsO_4(aq)$	– 249.3
8	$As_2O_3(s) + 6OH^-(aq) + O_2(g) \rightarrow 2AsO_4^{3-}(aq) + 3H_2O(l)$	– 487.2
9	$GaAs(s) + \frac{3}{2}H_2O_2(aq) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}Ga_2O_3(s) + \frac{1}{2}As_2O_3(s) + \frac{3}{2}H_2O(l)$	– 873.7
10	$AsH_3(g) + 2H_2O_2(aq) + O_2(g) \rightarrow H_3AsO_4(aq) + 2H_2O(l)$	–1043.3
11	$AsH_3(g) + 2H_2O_2(aq) + 3OH^-(aq) + O_2(g) \rightarrow AsO_4^{3-}(aq) + 5H_2O(l)$	–1296.4
12	$AsH_3(g) + 3OH^-(aq) + 2O_2(g) \rightarrow AsO_4^{3-}(aq) + 3H_2O(l)$	– 956.1
13	$GaAs(s) + H_2O_2(aq) + 3H^+(aq) + O_2(g) \rightarrow Ga^{3+}(aq) + HAsO_2(aq) + 2H_2O(l)$	–834.2
14	$GaAs(s) + 2H_2O_2(aq) + 3H^+(aq) + \frac{1}{2}O_2(g) \rightarrow Ga^{3+}(aq) + H_3AsO_3(aq) + 2H_2O(l)$	–937.3
15	$GaAs(s) + 2H_2O_2(aq) + 3H^+(aq) + O_2(g) \rightarrow Ga^{3+}(aq) + H_3AsO_4(aq) + 2H_2O(l)$	–1199.7
16	$H_2O_2(aq) + OH^-(aq) \rightarrow HO_2^-(aq) + H_2O(l)$	– 13.2
17	$GaAs(s) + 4HO_2^-(aq) \rightarrow Ga(OH)_4^-(aq) + AsO_4^{3-}(aq)$	–1331.4

9), arsenic acid (or arsenious acid, O=As(OH)$_3$, CAS no. 7778-39-4), and conjugate bases such as $H_2AsO_4^-(aq)$, $HAsO_4^{2-}(aq)$, $AsO_4^{3-}(aq)$, and $H_2AsO_3^-(aq)$. Reactions 10 to 15 in Table I depict the formation of these species.

Reactions of GaAs with H_2O_2 result in a significant decrease in the Gibbs free energy of reaction, indicating greater feasibility of GaAs oxidation in the presence of H_2O_2. Reaction 9 shows the formation of the oxides of Ga and As in the presence of H_2O_2. H_2O_2 is also expected to react with AsH_3, as shown in reactions 10 and 11, which would lead to a lower evolution of the AsH_3 gas than the amount produced by reactions such as 5 and 6. However, $AsH_3(g)$ can form water-soluble species even in the absence of H_2O_2, as depicted in reaction 12.

The two reactions that are particularly important in explaining the experimentally observed dissolution results are reactions 16 and 17 that occur in basic solutions. The first is the formation of the HO_2^- anion by deprotonation of H_2O_2, and the second is the reaction of GaAs with HO_2^- to form $Ga(OH)_4^-$ and AsO_4^{3-}. Reaction 15 has a $\Delta_{rxn}G^\circ$ value of -1331.4 kJ mol^{-1}, indicating a high thermodynamic propensity.

The reactions of GaAs and AsH_3 with H_2O_2 (cf. reactions 8 to 13) can occur under both anaerobic and aerobic conditions, but the presence of oxygen significantly increases the thermodynamic feasibility (on the basis of the more negative $\Delta_{rxn}G^\circ$ values).

In the following sections, data acquired using surface characterization techniques such as XPS and contact angle goniometry are used to discuss the observed trends in GaAs dissolution rates, removal rates, and AsH_3 evolution, on the basis of the reactions described in section 3.1.

Dissolution rates.— Chemical dissolution rates of GaAs (without mechanical polishing) were determined over a period of 30 min at 40°C, at different pH values in the range of 2 to 12, in aqueous solutions of H_2O_2 (0.3 M), sodium iodate (3 mM), and sodium periodate (3 mM). No measurable dissolution rates were observed in sodium iodate and sodium periodate solutions in the pH range of 2−12 and in H_2O_2 solutions in the pH range of 2−8. However, dissolution rates of about 150 and 620 nm min^{-1} measured in aq. H_2O_2 at pH 10 and pH 12, respectively. The low dissolution rates over pH 2−8 are evidently due to the formation of a passivating layer of Ga_2O_3, which is stable over this pH range, as discussed in the preceding section.

The standard Gibbs energy of reaction reported in Table I indicate that $\Delta_{rxn}G^\circ$ is significantly negative for reactions at both acidic and basic pH values. However, a higher dissolution rate was measured in basic pH values, indicating that the salts of $Ga(OH)_4^-$ and GaO_3^{3-} that are formed in basic media are more easily removed from the surface into the aqueous phase than the salts of Ga^{3+} and $Ga(OH)^{2+}$ that are formed in acidic media.

In contrast to the low dissolution rates of GaAs observed in this work, high GaAs etch rates have been reported in aqueous mixtures of H_2O_2 and sulfuric acid, H_2O_2 and ammonia, sodium hypochlorite and ammonia, and in solutions containing 0.5–3.5 M H_2O_2.[6,19,20]

Furthermore, Bryce et al.[20] observed that chemical dissolution in H_2O_2 solutions at a given pH was higher when the pH was adjusted using ammonium hydroxide instead of sodium hydroxide. For example, using a 1.2 M aq. H_2O_2 solution at pH 10.55, the etch rate was about 3000 nm min^{-1} when the pH was adjusted using ammonium hydroxide, and about 1000 nm min^{-1} when sodium hydroxide was used. They proposed that ammonia formed soluble complexes with oxidized Ga and As species, which resulted in the enhanced etch rates, and that these ammine complexes could not form when the pH was adjusted using sodium hydroxide.

The reason for lower dissolution rates in the dissolution experiments of the present study is that the concentration of H_2O_2 was only 0.3 M. The concentration of H_2O_2 used in the polishing experiments was even lower (3 mM). Low dissolution rates are desirable for better control of surface roughness during CMP.

The observed dissolution rates and their contribution to the overall material removal rates in CMP will be described in the following section.

GaAs removal rates: Role of oxidizing agents and silica.— Figure 1 shows the effect of different oxidizers (H_2O_2, sodium iodate and sodium periodate), at an arbitrarily chosen concentration of 3 mM, on GaAs RRs in the pH range of 2–12 using Nexsil 35A silica dispersions (3 wt%). The error bars represent the standard uncertainty of the gravimetric measurements. The RRs were low (below about 60 nm min^{-1}) over the entire pH range when a dispersion of just the silica particles was used. However, the RR increased significantly (up to about 1500 nm min^{-1}) because of the oxidizer. Sodium iodate and sodium periodate yielded higher removal rates than H_2O_2 in acidic media (cf. Figure 1). For both of these oxidizers, removal rates decreased with an increase in the pH of the aqueous phase. These observations are

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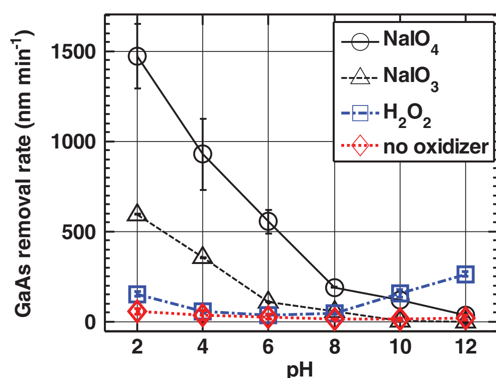
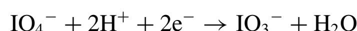


Figure 1. GaAs removal rates as a function of pH during CMP using aq. dispersions of Nexsil 35A silica particles alone (3 wt%) and in the presence of the oxidizers, hydrogen peroxide, sodium periodate and sodium iodate, all at 3 mM concentration.

consistent with the fact that an acidic pH is necessary for iodate and periodate to act as oxidizers, as depicted in the following reactions.

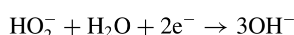
$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$$



$$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$$

In contrast, H_2O_2 can act as an oxidizer in both acidic and basic media, as shown in the following two reactions:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$



$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$$

Here the hydroperoxide anion, HO_2^-, is produced by the reaction between H_2O_2 and OH^-(reaction 16, Table I). Thus, H_2O_2 resulted in measurable removal rates in both acidic (pH 2) and basic (pH 10 and 12) slurries.

In spite of the stronger oxidizing effect of the iodate and periodate oxidizers in acidic pH, H_2O_2 is the preferred choice in most semiconductor applications because of the relatively clean by-products (oxygen or water). Although the effect of H_2O_2 on GaAs removal was relatively low at 3 mM concentration, the removal rate increased significantly with an increase in the concentration of H_2O_2, particularly at pH 10 (cf. Figure 2).

Based on the data in Figure 2, a H_2O_2 concentration of 0.3 M was chosen for all subsequent experiments. The GaAs RRs at pH 2 and pH 10 were reasonable at this concentration of H_2O_2, whereas the dissolution rates were negligible—both prerequisites for effective planarization of patterned structures.

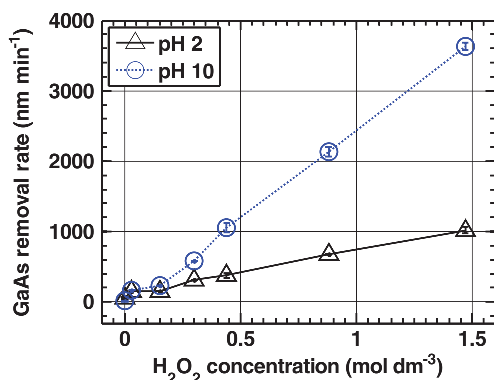


Figure 2. The effect of H_2O_2 concentration, over a range of 0 to 1.47 M, in aq. dispersions of Nexsil 35A silica particles (3 wt%), at pH 2 and pH 10, on the removal rates of GaAs.

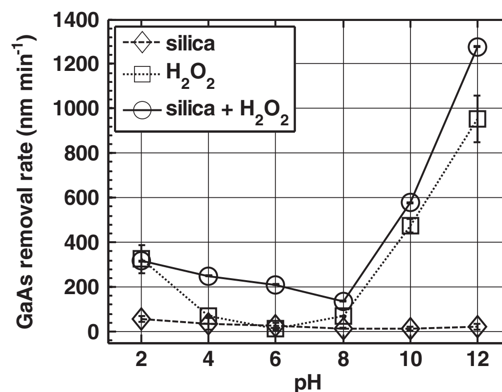


Figure 3. Material removal rates during CMP of GaAs, at different pH values of the aqueous phase, using: (a) an aq. dispersion of Nexsil 35A silica particles (3 wt%); (b) an aq. H_2O_2 solution of 0.3 M concentration; and (c) an aq. dispersion of Nexsil 35A (3 wt%) containing H_2O_2 (0.3 M).

Figure 3 shows the effect of silica abrasives on GaAs RRs. When the slurry contained only the silica particles and no H_2O_2, the GaAs RRs were very low in the pH range of 2 to 12. Indeed, the silica particles were not effective even in the pH interval of 2-6 in spite of the electrostatic attraction between them and the GaAs (isoelectric point ≈ 6)[22] surface.

In contrast, the GaAs removal rates were significantly higher when the polishing was performed using an abrasive-free aqueous solution of H_2O_2 (0.3 M). The removal rates were significantly higher at pH values of 10 and 12 than at the pH value of 2, and relatively low in the intermediate pH range.

Removal rates using slurries containing both the abrasive (3 wt% Nexsil 35A) and 0.3 M aq. H_2O_2 were also studied. They showed similar dependence on pH as those obtained using abrasive-free solutions of 0.3 M aq. H_2O_2 and the RRs were only slightly higher when the abrasive particles were added, especially in the pH range 8 to12. Thus, it appears that in this pH range the shear stress generated by the polishing pad alone seems to be sufficient to polish the oxidized GaAs surface, with no major benefit arising from the abrasive particles. The increase in GaAs RRs between pH 2 and 6 in the presence of H_2O_2 and silica particles may be due to the electrostatic attraction between the negatively charged silica particles and the positively charged Ga_2O_3, with an isoelectric point of ~ 9,[23] formed in the presence of H_2O_2 as discussed above and implies that this oxide is relatively weakly bound to the underlying GaAs substrate.

The high RRs of GaAs, in highly basic solutions can be attributed to the hydroperoxide anion, HO_2^- (see reactions 16 and 17 in Table I). However, the concentration of HO_2^- is expected to small at pH values below about 10, which is evidently the reason for the lower removal rate when the pH value is below 10 (cf. Figure 3).

Additionally, in slurries containing H_2O_2, a large amount of KOH was required to adjust the pH of the aqueous phase to basic values. For example, with 1 L of a slurry containing 3 wt% Nexsil 35A silica particles and no H_2O_2 (natural pH $\sim$3), about 0.002 and 0.012 moles of KOH were required to adjust the pH of the slurry to 10 and 12, respectively. In contrast, when the slurry contained 0.3 M H_2O_2 (natural pH $\sim$4), approximately 0.08 and 0.24 moles of KOH were required to attain these pH values. Clearly, a significant amount of KOH was being consumed in reaction 16 (cf. Table I). The high concentrations of KOH would increase the ionic strength of the slurries and contribute to the enhancement in removal rates, similar to our observations for Ge and SiC removal[22,24] and during nanowear of silica surfaces in electrolyte solutions.[25] Indeed, when KCl or KNO_3 salts were added (in 0.1 M concentration) to a slurry containing 0.3 M H_2O_2 and 3 wt% silica particles at pH 10, the GaAs removal rate was found to increase from 580 nm min^{-1} to about 750 nm min^{-1}.

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Polished GaAs surface quality.— The RMS surface roughness of the as-received GaAs wafer samples was ~0.2 nm and increased to ~0.5 nm when polished with a pH-4 silica slurry containing 0.3 M H_2O_2 and further to ~0.7 nm when the pH of the slurry was 2. Thus, additional development work is required for channel applications that require ultra-smooth surfaces. As will be discussed in section 3.7, solutions containing H_2O_2 oxidizer caused preferential removal of As from the GaAs surface, which could be a factor affecting surface quality. The incorporation of a complexing agent such as oxalic acid[4] in the slurry, to promote the removal of Ga species, might help in a more uniform material removal, and, therefore, in achieving a lower surface roughness.

Arsenic trihydride evolution.— No AsH_3 evolution was detected during the polishing of GaAs films using any of the investigated slurries, over a pH range of 2 to 12. AsH_3 evolution was also negligible in slurries that did not contain H_2O_2, iodate, or periodate. In contrast, the dissolution of InP, another III-V material, resulted in measurable evolution of PH_3 gas.[4] The solubility of AsH_3 in water is significantly higher than that of PH_3 in water. Using the Henry's law constant for water solubility of AsH_3 and PH_3,[26] the solubility of these gases at 25°C and 1 bar pressure were estimated to be 0.69 and 0.27 g/L, respectively. Thus, it is likely that the amount of AsH_3 formed was below its solubility limit in the aqueous phase of the slurry.

Although AsH_3 formation is expected on the basis of reactions such as 5 and 6 (cf. Table I), $\Delta_{rxn}G^\circ$ for these reactions are relatively high. Therefore, these reactions are expected to proceed to any significant extents only at low pH (near 0) and high pH (near 14), respectively. Based on the results of our experiments, it is evident that even if any AsH_3 is formed during the CMP, it remains dissolved or undergoes further reaction in the slurry and its release as a gas is negligible.

Nevertheless, AsH_3 evolution was detected in some dissolution experiments that were carried out for a longer duration of 30 min at 40°C. In dissolution studies (without mechanical polishing) no $AsH_3(g)$ was detected when either sodium iodate or sodium periodate was used as the oxidizer, at a concentration of 0.3 M, over a pH range of 2 to 12. However, $AsH_3(g)$ was detected when 0.3 M H_2O_2 was used (cf. Figure 4). In etching solutions containing 0.3 M H_2O_2, the mass of AsH_3 evolved was higher in acidic (pH 2) and basic (pH 10 and 12) solutions, but lower in solutions with the intermediate pH values of 4, 6, and 8 (cf. Figure 4). $AsH_3(g)$ evolution was lower from a solution of pH 10 compared with a solution of pH 12, evidently because of reactions such as 11 and 12 (Table I) that fix arsenic in the solution in the form of $AsO_4^{3-}(aq)$ [see reaction 12 in Table I that requires OH^- and results in the consumption of AsH_3 (g)].

Surface wettability.— The static contact angle of deionized water on GaAs surface was 73°. The contact angle decreased to 63° when the surface was dipped in acidic water (pH 2). The surface became significantly more hydrophilic, with water contact angles of 17 and 21°, when immersed in aq. H_2O_2 solutions of pH 2 and pH 10, respectively. The hydrophilicity is attributed to gallium and arsenic salts that are formed by the reaction of GaAs with H_2O_2, but are insoluble and remain attached to the surface. The presence of such salts was further confirmed using X-ray photoelectron spectroscopy.

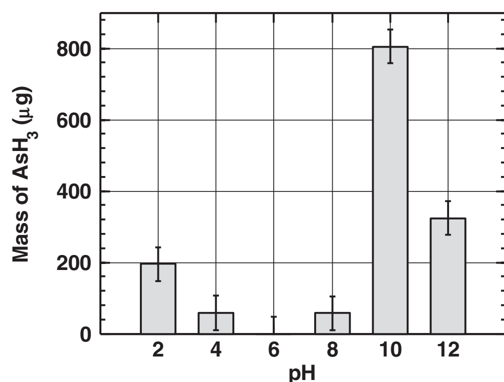

Figure 4. Mass of AsH_3 generated during dissolution of GaAs in aqueous solutions containing hydrogen peroxide (0.3 M) at 40°C over a period of 30 min at different pH values of the solution.

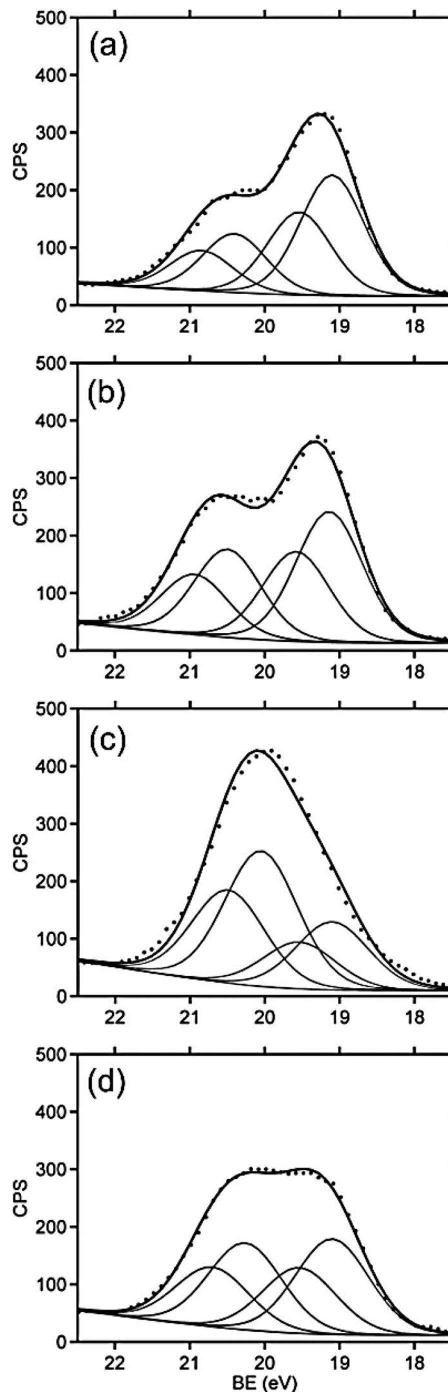

Figure 5. Ga 3d XPS spectra for (a) as-received GaAs wafer, (b) GaAs wafer immersed in acidic aq. H_2O_2 (0.3 M, pH 2), (c) GaAs wafer immersed in basic aq. H_2O_2 (0.3 M, pH 10), and (d) GaAs wafer immersed in acidic aq. sodium periodate (3 mM, pH 2), acquired at emission angles of 56°.

X-ray photoelectron spectroscopy.— Figure 5 shows the Ga3d XPS spectra of the surfaces of as received GaAs wafer, a GaAs surface

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dipped in aq. H_2O_2 solutions (0.3 M) of pH 2 and pH 10, and a GaAs surface dipped in an acidic (pH 2) aq. solution of $NaIO_4$ (3 mM).

Curve fitting was performed using the Tougaard background[27] and symmetric Gaussian-Lorentzian-product peak shape functions with a Lorentzian content of about 15%. The spectra were fitted using the Ga $3d_{5/2}$ and $3d_{3/2}$ doublets, and the binding energy was corrected using a value of 19.1 eV for the Ga $3d_{5/2}$ peak. The ratio of the Ga $3d_{3/2}$ and Ga $3d_{5/2}$ peak areas was constrained to a value of 0.687, corresponding to the ratio of the corresponding relative sensitivity factors. The spin orbit splitting of the Ga $3d_{5/2}$ and Ga $3d_{3/2}$ energy levels was constrained to 0.44 eV.

The spectrum of the as-received sample clearly shows the presence of oxidized species, such as Ga_2O_3,[28] with binding energy in the range of 20 to 21.5 eV. The surface concentration of oxidized species was significantly higher in samples treated with solutions containing the oxidizers, H_2O_2 or $NaIO_4$. The area percentage of the Ga 3d spectrum corresponding to oxidized species was ~32.8% for the surface of as received GaAs, ~43.6% for the GaAs surface treated with an acidic aq. solution of H_2O_2 (0.3 M, pH 2), ~~100%~~ for the GaAs surface treated with a basic aq. solution of H_2O_2 (0.3 M, pH 10), and ~47.7% for the GaAs surface treated with an acidic aq. solution of $NaIO_4$ (3 mM, pH 2).

Figure 6 shows the As 3d spectra of the same set of surfaces described above. The spectra were fitted with As $3d_{5/2}$ and As $3d_{3/2}$ doublets located 0.7 eV apart. All samples showed peaks corresponding to oxidized As species, such as As_2O_3, at binding energies in the range of 43 to 46 eV. The area percentage of the As 3d spectrum corresponding to oxidized species was 27.2% for the as received GaAs surface, 41.7% in the surface treated with the acidic aq. H_2O_2 solution, 100% in the surface treated with the basic aq. H_2O_2 solution, and 54.3% in the surface sample treated with acidic aq. solution of $NaIO_4$.

The integrated peak intensities and the relatively sensitivity factors of 1.09 and 1.82 for the Ga 3d and As 3d peaks, respectively, were used to estimate the atomic ratios of Ga to As within the XPS probe depths of the analyzed surfaces. The results are summarized in Table II.

On the basis of the atomic ratios listed in Table II, the surface of the as received GaAs wafers contained Ga and As concentrations close to the stoichiometric ratio of 1. However, the Ga to As ratio at the surface increased significantly upon dissolution in a solution containing an oxidizer, suggesting preferential dissolution of As, particularly when the oxidant was H_2O_2 in 0.3 M concentration at pH 10. The results of our XPS analysis are consistent with the formation of relatively insoluble Ga_2O_3 and soluble arsenic species upon oxidation of GaAs in water, as discussed in ~~Section 3.1~~. The preferential dissolution of As over Ga was also confirmed using composition analysis of the post-CMP slurry components (solid and liquid phases) by X-ray fluorescence spectrometry.

X-ray fluorescence (XRF) spectrometry.— Elemental compositions of the slurries from two different polishing experiments, one at pH 2 and the other at pH 10, both using Nexsil 35A silica particles (3 wt%) and H_2O_2 (0.3 M) were analyzed using XRF spectrometry. Gravimetric analysis showed that 1243 μg of GaAs was polished using the pH-2 slurry and 2006 μg using the pH-10 slurry. The Ga and As concentrations in the solid and liquid phases of the slurry determined by XRF spectrometry were then used to calculate the individual amounts of Ga and As removed from the surface at each pH value,

Table II. The ratios of integrated XPS peak intensities and atomic concentrations of Ga and As.

	Ratio of peak areas of Ga to As	Ratio of surface atomic concentrations of Ga to As
As received GaAs surface	0.70	1.17
GaAs surface treated with acidic aq. H_2O_2 (0.3 M, pH 2)	0.86	1.43
GaAs surface treated with basic aq. H_2O_2 (0.3 M, pH 10)	1.52	2.54
GaAs surface treated with acidic aq. $NaIO_4$ (3 mM, pH 2)	0.95	1.58

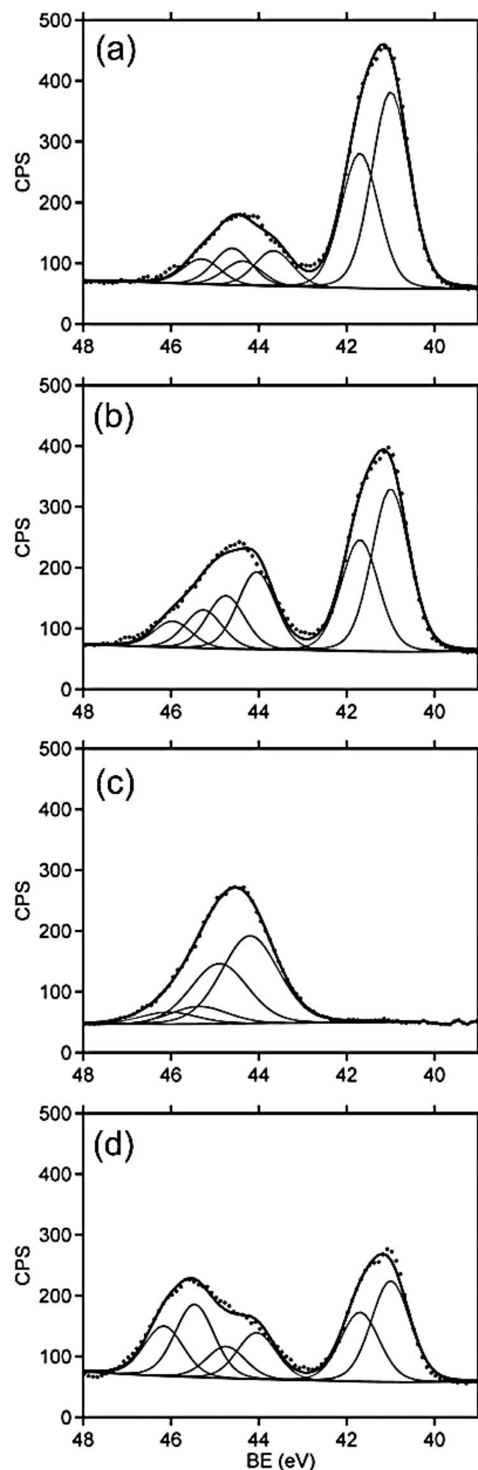

Figure 6. As 3d XPS spectra for (a) as-received GaAs wafer, (b) GaAs wafer immersed in acidic aq. H_2O_2 (0.3 M, pH 2), (c) GaAs wafer immersed in basic aq. H_2O_2 (0.3 M, pH 10), and (d) GaAs wafer immersed in acidic aq. sodium periodate (3 mM, pH 2); acquired at emission angles of 56°.

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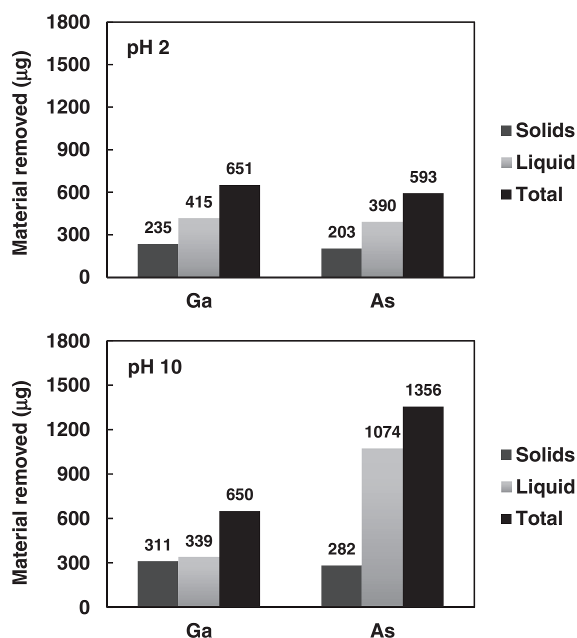

Figure 7. Amounts of Ga and As associated with the solid and liquid phases of the post-CMP slurry, calculated using the concentrations of Ga and As in the solid and liquid phases, determined using X-ray fluorescence spectrometry. Data for two different slurries, each containing 3 wt% Nexsil 35A silica particles and 0.3 M H_2O_2, with pH values of 2 (top) and 10 (bottom) are shown.

and their partitioning between the solid and liquid phases of the slurry. The results are shown in Figure 7.

It is evident from Figure 7 that the amount of As in the pH-10 slurry was significantly higher than that in the pH-2 slurry, consistent with the higher material removal using the pH-10 slurry. The total amount of Ga in the post-CMP slurry was almost the same for the pH-2 and pH-10 slurries (about 650 µg). The greater removal of As from the GaAs surface into the slurry is consistent with the XPS data that showed a higher Ga to As ratio (2.54) in the surface polished using the pH-10 slurry than in the surface polished using the pH-2 slurry (1.43). Thus, both XPS and XRF data indicate that As removal is significantly higher than Ga removal in basic aq. H_2O_2 slurries, whereas in acidic slurries, this difference is smaller.

Obviously, nonselective removal of both Ga and As is essential during polishing and planarization. Hence, while further investigation involving patterned wafers is necessary, neutral or slightly acidic silica slurries containing H_2O_2 seem to be optimal for CMP of GaAs, because of the negligible GaAs dissolution rates in these slurries and negligible evolution of AsH_3 gas. Of course, while toxic AsH_3 evolution is minimized, proper disposal of all As-containing post-polish slurry constituents and pads remains paramount.

Conclusions

The calculation of the standard free energy of reactions indicated that the formation of the oxides of Ga and As is thermodynamically feasible in the aqueous solutions used for the polishing of GaAs surfaces. Ga_2O_3 dissolved in acidic and basic solutions by the formation of Ga^{3+} and $Ga(OH)_4{}^-$ salts, respectively. As_2O_3 is expected to be soluble over the entire pH range because of the formation of species such as $HAsO_2$, H_3AsO_4, and $AsO_4{}^{3-}$.

In the absence of mechanical polishing, chemical dissolution of GaAs in aqueous solutions of oxidizers such as $NaIO_3$, $NaIO_4$, and H_2O_2 of 3 mM concentration is negligible except in solutions of H_2O_2 at pH 10 and pH 12, attributed to the formation of a passivating layer of relatively stable Ga_2O_3.

During chemical mechanical polishing using silica abrasives, the oxidizers $NaIO_3$ and $NaIO_4$ were found to be much more effective in GaAs removal than H_2O_2 at equal molar concentrations (3 mM). In slurries containing H_2O_2, GaAs removal increased with an increase in the concentration of H_2O_2. The removal was higher in basic solutions than in acidic solutions.

The chemical mechanical polishing of GaAs with an aqueous dispersion of silica particles containing 0.3 M H_2O_2 in acidic pH resulted in a satisfactory material removal rate, of approximately 300 nm min^{-1}, with almost no evolution of the toxic arsenic trihydride gas, but the post-CMP slurry must be carefully handled because of the accumulation of the arsenic removed from the surface.

Although the formation of arsenic trihydride is thermodynamically feasible by the reaction of GaAs in both acidic and pH aq. solutions, AsH_3 expected to undergo further reactions particularly in the presence of oxidizers such as H_2O_2 to form water soluble species. The evolution of $AsH_3(g)$ was found to be negligible in CMP of GaAs surfaces, carried out for a period of 1 min. However, in dissolution experiments performed over a longer duration of 30 min, the evolution of $AsH_3(g)$ was higher in aq. basic solutions of H_2O_2 than in aq. acidic solutions.

X-ray photoelectron spectroscopy indicates that the surfaces of GaAs were richer in Ga than As. Etching of GaAs surfaces using pH 10 aq. H_2O_2 solutions resulted in significant depletion of As from the surface relative to Ga. Almost all of the residual As was found to be in the oxidized form. The preferential removal of As from the surface was also evident in the X-ray fluorescence spectrometry of the post-CMP slurries which showed a higher total concentration of As in the solid and liquid phases of the slurry than the total concentration of Ga. Thus, further development work is necessary to minimize post-polish surface roughness.

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