Effects of pH Values on the Kinetics of Liquid-Phase Chemical-Enhanced Oxidation of GaAs

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The liquid-phase chemical-enhanced oxidation technique has been demonstrated to be an effective means of growing stable native films on GaAs. The gallium-ion-containing solution results in a fairly high oxidation rate near room temperature. The pH value of the oxidation solution appears to be a dominant factor in the kinetics of oxidation. Due to the enhancement of Ga-containing cations in the solution, a window of initial pH values from approximately 4.0 to 4.5 is found to be the optimum pH range for oxide growth. The pH-incorporated mechanism provides consistent interpretations for the unusual experimental results such as etchback of oxide thickness and increase of refractive index. In addition, the results of the pH-controlled procedure confirm the proposed role of pH. According to secondary ion mass spectrometry profiles, it is found that the increasing As/Ga ratio of the oxide film contributes to the increase of oxide refractive index.

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Due to their technological importance, native films on III-V semiconductors have been studied intensively.1 Investigations of thermal or anodic oxides on GaAs have been performed for a number of years.2-4 Many inherent problems in these two oxidation methods need to be overcome as they are applied to GaAs metal oxide semiconductor (MOS) technologies. In the case of anodic oxidation, a high electric field (~5 MV/cm) in oxide films cause Ga and As atoms to diffuse through the oxide layer to the surface where they are oxidized.5 It has also been reported that growth of anodic oxides are initiated by the reactions on the oxide surface.6 Therefore, anodic oxidation is sensitive to contamination of the GaAs surface. As compared to the anodic method, the advantage of thermal oxidation is that it generates a fresh interface with surface contamination ending up at the oxide surface, since thermal oxidation takes place at the interface by in-diffusion of oxygen.7 However, oxidation of GaAs proceeds very slowly below 450°C (<50 Å/h).8 In addition, because the oxidation temperature exceeds the volatile temperature of As2O3, thermal oxides are composed of mostly Ga2O3. These results lead to loss of stoichiometry both in the oxide films and at the interface. At higher temperatures (>530°C), the films tend to crystallize and become porous, and even incongruent evaporation from substrates possibly occurs. Extensive efforts have been made to overcome this problem, such as high-pressure,2,9 photoassisted,10 plasma-enhanced,11 or steam oxidation12 methods. Among the above techniques, the required systems are complex, or the temperatures are still high.

Recently, a new liquid-phase chemical-enhanced oxidation (LPCEO) technique has been proposed.13 Neither photoenergy nor plasma source is needed. As compared to the anodic method, oxide films of GaAs can be grown near room temperature (40-70°C) without the assistance of electric potential. Featureless and uniform oxide films can be grown at a relatively high oxidation rate (~1000 Å/within an hour). In addition, good insulating and thermally stable LPCEO oxide films have been demonstrated,14 and device applications to GaAs metal-oxide semiconductor field effect transistors (MOSFETs) have also been realized.15 Interesting properties of the oxide growth kinetics of the LPCEO technique have been found, such as an optimum pH window for oxide growth, increase of oxide refractive index, a relatively high oxidation rate at low temperature, and etchback of oxide thickness. The experimental results indicate that the pH value of oxidation solution seems to be the dominant factor in oxide growth. In this work, the mechanisms of the Ga-containing cations as well as the role of the pH value in the LPCEO technique are investigated.

Experimental

Figure 1a illustrates the oxidation system which is very low cost and mainly consists of a temperature regulator and a pH meter. The flowchart of the procedure is shown in Fig. 1b. The LPCEO procedure is started with the preparation of oxidation solutions. First, a gallium ion-containing nitric acid solution is obtained by dissolution of Ga metal in nitric acid solution.
of high purity (8 N) gallium metal 25 g in hot (60°C) nitric acid (70%) 200 mL for a few hours

$$2\text{Ga}_{(s)} + 6\text{HNO}_3(aq) \rightarrow 2\text{Ga(NO}_3)_3(aq) + 3\text{H}_2\text{O}$$  \[1\]

and then diluted by deionized water (DI water) to a volume ratio of 1:10. Then, the pH adjustment process is performed by adding ammonia water solution ($\text{NH}_4\text{OH}$:DI water = 1:10) at room temperature. The reaction is

$$\text{Ga(NO}_3)_3(aq) + 3\text{NH}_4\text{OH}(aq) \rightarrow 3\text{NH}_4\text{NO}_3(aq) + \text{Ga(OH)}_3(s)$$  \[2\]

White precipitates (mainly gallium oxide or hydroxide) are generated during pH adjustment, then they are dissolved rapidly into the solution at pH < 4. While the pH value of the solution is close to pH 4, the solution starts to become muddy. Finally, a clear solution is obtained by filtration and ready for use. As is discussed later, the pH value of solution decreases with oxidation time, and the initial pH value (pH$_i$) within a range from 4 to 4.5 is found to be the optimum condition for oxidation.

The GaAs wafers are cleaned by organic solvents (2-propanol, acetone, methanol) and etched in $\text{H}_2\text{SO}_4$:$\text{H}_2\text{O}_2$:$\text{H}_2\text{O}$ (4:1:1). After that, the NH$_4$OH solution (10-20% concentration) is employed to etch residual native oxide, and then the wafer is immediately immersed into the oxidation solution at a constant temperature. Finally, the as-oxidized samples are dried in nitrogen and soaked in methanol to keep from air exposure. The thickness and refractive index of the oxide films are measured by a Rudolph Auto El-III ellipsometer using a visible laser ($\lambda$ = 633 nm) as the incident beam.

### Results and Discussion

#### General results

Figure 2a shows the plot for the oxide film thickness as a function of oxidation time at 70°C. The pH$_i$ value is adjusted to pH$_i$ = 4.3 within the optimum window, and then the pH value decreases when oxidation begins. The oxide layer thickness increases with increasing time, however, the oxidation rate saturates significantly for longtime oxidation (about 3 h), that is, it reveals a nonlinear relation between oxide thickness and oxidation time. Saturation of oxide growth has been found in other oxidation techniques such as the photothermal oxidation of GaAs in water or aqueous solutions. However, the difference of LPCEO technique from the above approaches is that the oxide film appears to be etched back after saturation. Moreover, it has also been found that the refractive index of oxide film increases obviously for long oxidation time, especially when the pH values decrease out the pH window (approx. 4.5-3). A high refractive index (~2.3) of oxide film can be obtained at 70°C for 4 h. The increase of the refractive index implies that the larger amount of Ga cations the solution contains, the higher density the solution has. Figure 2b shows the relation of relative solution densities between their pH values. The densities are obtained with dividing the solution weight by its volume. The weight and volume of the solutions are measured by precision meters. It has been found that our assumption is consistent with the prediction from the equilibrium phase diagram, so that it cannot be the accumulation of some species within the oxide film. As is discussed later in this article, the increase of refractive index is contributed by increasing As/Ga ratio of the oxide film. For comparison, Fig. 2b shows the results in the case of pH$_i$ outside the optimum window (pH$_i$ = 5.4). Delay of oxide growth at the beginning of oxidation has been clearly observed. If oxidation is initiated at higher pH values (higher than the optimum pH$_i$ window), the pH value will decrease more significantly than that inside the optimum pH$_i$ window.

#### Hydrolytic behavior of the oxides and cations

Before investigating the effects of pH on oxide growth, the natures of GaAs oxide components in aqueous solutions should be considered. $\text{As}_2\text{O}_3$ is moderately soluble in water, but dissolves easily in an alkaline solution to produce a solution of arsenite, $\text{As}_2\text{O}_4^{3-}$ or $[\text{Ga(OH)}_2]^+$ and solid gallium hydroxide oxide $[\text{GaO(OH)}]$. We refer to the Ga polycation as a “quasi-oxidized cation” throughout this paper. In order to verify the existence of the hydroyzed Ga cations in the solution, we assume that the larger amount of Ga cations the solution contains, the higher density the solution has. Figure 2 shows the experimental relation of relative solution densities between their pH values. The densities are obtained with dividing the solution weight by its volume. The weight and volume of the solutions are measured by precision meters. It has been found that our assumption is consistent with the prediction from the equilibrium phase diagram, so that it cannot be the accumulation of some species within the oxide film. As is discussed later in this article, the increase of refractive index is contributed by increasing As/Ga ratio of the oxide film. For comparison, Fig. 2b shows the results in the case of pH$_i$ outside the optimum window (pH$_i$ = 5.4). Delay of oxide growth at the beginning of oxidation has been clearly observed. If oxidation is initiated at higher pH values (higher than the optimum pH$_i$ window), the pH value will decrease more significantly than that inside the optimum pH$_i$ window.

#### Oxidation Temperature

- **Oxidation Temperature = 70°C**
  - pH$_i$ = 4.3
  - pH$_i$ = 5.4

Based on a previous report, a gallium polycation species ($[\text{GaO}_2\text{Ga}_2(\text{OH})_3\text{H}_2\text{O}]^{2+}$) forms during the hydrolysis of gallium(III) solutions in the pH range of approximately 3-4. The above pH range is very close to that in the present oxidation method (decreased from 4.5 to 3.5). Since it is an intermediate species between soluble gallic ($\text{Ga}^{3+}$) or $[\text{Ga(OH)}_2]^+$ and solid gallium hydroxide oxide $[\text{GaO(OH)}]$, we refer to the Ga polycation as a “quasi-oxidized cation” throughout this paper. In order to verify the existence of the hydroyzed Ga cations in the solution, we assume that the larger amount of Ga cations the solution contains, the higher density the solution has. Figure 2 shows the experimental relation of relative solution densities between their pH values. The densities are obtained with dividing the solution weight by its volume. The weight and volume of the solutions are measured by precision meters. It has been found that our assumption is consistent with the prediction from the equilibrium phase diagram, so that it cannot be the accumulation of some species within the oxide film. As is discussed later in this article, the increase of refractive index is contributed by increasing As/Ga ratio of the oxide film. For comparison, Fig. 2b shows the results in the case of pH$_i$ outside the optimum window (pH$_i$ = 5.4). Delay of oxide growth at the beginning of oxidation has been clearly observed. If oxidation is initiated at higher pH values (higher than the optimum pH$_i$ window), the pH value will decrease more significantly than that inside the optimum pH$_i$ window.
the existence of quasi-oxidized cation in solution enhances the oxidation reactions, and they dissolve into solution continuously, i.e., the solution pH is within the window for the fast oxidation rate. Although the oxidation reaction proceeds in a pH adjusted (pH > 4) nitric acid solution without the addition of ammonia, the existence of quasi-oxidized cation in solution enhances the oxidation reactions. As a result, the optimum pH range for oxide growth should be close to but lower than pH 5. The experimental result (optimum pH 4 < pH < 4.5) shows good agreement with the above speculations.

Effects of hydrolyzed gallium cations.—Figure 3 shows the film thickness of the oxides grown within an hour as a function of pH. A pH window for fast oxidation rate can be seen clearly. While the oxidation solution contained a large amount of quasi-oxidized Ga cations, i.e., 4 < pH < 4.5, the oxidation reaction appears to be rapid at the beginning of oxidation (~850 Å for 1 h at 70°C). A possible contribution to this reaction is that the quasi-oxidized Ga cation species is adsorbed on the GaAs surface as a precursor for enhancing the oxide growth by accelerating the transfer of oxidizing species (O₂, H₂O, NO₂, etc.) into GaAs. In contrast, if the pH of solutions is elevated to higher values (pH > 5, refer to Fig. 2b), the oxidation reaction is significantly delayed because the concentration of the quasi-oxidized Ga cation in the oxidation solution at higher pH values is much lower than that within the pH window. In the case of low pH (pH < 4), the metallic Ga atoms are in the form of soluble ions, and they dissolve into solution continuously, i.e., the solution is undersaturated with Ga oxides. Consequently, as the Ga atoms at GaAs surface are dissolved by the solution, the oxidation will be turned into etching.

Nitric acid is a strong oxidizing reagent, and it oxidizes many kinds of semiconductor materials. However, at the same time, dissolution of oxide into the nitric acid solution is rapid due to the extremely low pH environment. For example, in the case of the oxides of GaAs, gallium oxides transform to soluble gallic (Ga-OH) and [Ga(H₂O)₆]⁺⁺ and dissolve into the solution at low pH values. Therefore, it is difficult to obtain a thick oxide film (>100 Å) on GaAs wafers with a pure or diluted nitric acid solution. The interpretations indicate not only the reasons that oxide films cannot be grown at low pH, but also why the oxide film is etched back for a long oxidation time. In other words, the pH value of the solution decreases, and the oxide starts to be etched due to the low pH environment.

In addition, we have also found that the oxidation reaction still proceeds in a pH adjusted (pH > 4) nitric acid solution without the Ga-containing quasi-oxidized cations. However, the oxidation rate is very low (<200 Å for 1 h) similar to the results of oxidation at high pH. Since the etching (dissolution) of oxidized substance into solution can be weakened by elevating the pH value, so that a thick (>1000 Å) oxide film can be grown in pH-adjusted nitric acid for longer oxidation time. As a result, it can be concluded that the quasi-oxidized Ga cations play the role of a catalyzer of oxide growth.

Accumulation of As compounds.—The increase of refractive index of oxide film with oxidation time is interesting. In order to investigate the mechanism, we use secondary ion mass spectroscopy (SIMS) using a CAMECA IMS-5F system with double focusing mass spectrometer are used for analysis of oxide films. Sputtering is performed using O₂⁻ (12.5 keV) as the primary ion beam. Mass peaks M⁺ = 75 (As⁺⁺) and M’ = 69 (Ga⁺⁺) are recorded. For quantitative analysis of As concentration in oxide films, the samples are measured in the same conditions, and relative counts of As and Ga are calibrated with respect to the As/Ga count ratio of GaAs substrates. For analysis, we use SIMS depth profiles of the oxide films which have refractive indexes of 1.55, 2.03, and 2.25, respectively. Figure 5 shows the estimated and calibrated As/Ga ratio as a function of sputtering time of the corresponding samples. It is clearly seen that when the oxide film has a higher refractive index, the As/Ga ratio of the oxide film is higher. Based on our previous works, the surface of the oxide film is determined to be composed of Ga₂O₃ and As₂O₃. X-ray photoelectron spectroscopy (XPS). XPS depth profiles indicate that these accumulated arsenic compounds in the oxide films are a mixture of As₂O₃ and elemental As. If the pH of the oxidation solution decreases toward more acidic values, then the dissolution of As and As₂O₃ into the solution will be suppressed. Therefore, it is reasonable that As and As₂O₃ accumulate within the oxides grown at lower pH solutions, which leads to the increase of the refractive index. As discussed before, both
As and \( \text{As}_2\text{O}_3 \) are more insoluble in acid solutions. Agreement between the hydrolytic behaviors of these two species with the above results seems to be good. On the other hand, due to the insolubility of elemental As in both the acid or base solutions we presume that the higher accumulation of \( \text{As}_2\text{O}_3 \) in the oxide at low pH oxidation solution is the major contribution to the increase of the As/Ga ratio and the refractive index.

The \( \text{pH} \) controlled procedure.—In order to confirm the proposed role of \( \text{pH} \), we have performed a “pH controlled” procedure for oxidation in this study. The technique is to modify the \( \text{pH} \) value by introducing ammonia water into the oxidation solution periodically. The mixture of 1mL \( \text{NH}_4\text{OH} \) (28%) solution diluted with 300 mL DI water is employed as the controlling dose. During oxidation, a 0.1 mL controlling dose is added into the oxidation solution per 1 h to control the \( \text{pH} \) value within the window of 4 < \( \text{pH} \) < 4.5. The \( \text{pH} \) value increases rapidly during the use of the controlling dose, and then decreases with time. Figure 6a and b show the relationship of thickness and refractive index with oxidation time for \( \text{pH} \) controlled and normal (without the addition of controlling dose) procedures. The inset illustrates the \( \text{pH} \) variation during oxidation by the \( \text{pH} \)-controlled method.

Using the same oxidation system, we also employed Si or InP substrates in this work, and no thick native film could be grown. In the normal procedure, therefore, the oxide is not deposited from the oxide particles or cations in the solution but grown natively. However, the situation is different in the \( \text{pH} \)-controlled procedure. By the \( \text{pH} \)-controlled method, the linearity of oxide thickness vs. oxidation time is improved significantly. In addition, the refractive indexes of the oxide film within a constant range can be realized by the \( \text{pH} \)-controlled procedure. On the other hand, since the \( \text{pH} \) value is elevated, Ga hydroxide particles will generate during the \( \text{pH} \) control period. It is possible that the particles loosen and roughen the oxide film by the deposition processes (deposition of Ga oxide or hydroxide particles), therefore, both the As/Ga ratio and the refractive index are lowered. The above effects reveal a trade-off between the oxidation rate and the film density. Therefore, it is better to minimize the \( \text{pH} \) variation resulting from adding the controlling dose (\( \text{NH}_4\text{OH} \) solution) by shortening the control period. To conclude the above observations, the experimental results seem to confirm that the \( \text{pH} \) value of LPCEO technique is the dominant factor in oxide growth kinetics.

The model for oxidation kinetics.—A proposed model for the oxidation kinetics of the LPCEO technique is shown in Fig. 7. In the model, the experimental observations of (i) a high initial oxidation rate within optimum \( \text{pH} \) window, (ii) oxidation delay at high \( \text{pH} \), and (iii) the increasing As/Ga ratio of oxide films as the oxidation proceeds at lower \( \text{pH} \) values are incorporated. At the \( \text{pH} \) values in the range of 3 < \( \text{pH} \) < 5, the Ga-containing species go into three configurations in the aqueous solutions: gallic ion, polyoxycation, and hydroxide. As the \( \text{pH} \) values are within 4 to 4.5, the highest concentration of the polyoxycation appears to enhance the oxide growth at the beginning of oxidation. The possible contribution is the chemisorption of the polyoxycation on the GaAs surface, and the “quasi-oxidized cation” may act as a transportation bridge for the oxidizing species into GaAs. At higher \( \text{pH} \) values, the absence of the polyoxycation (transformed to the hydroxide) results in a low oxidation rate (weaker transfer of oxidizing species). The dissolution of As-related compounds (As, \( \text{As}_2\text{O}_3 \)) into solution at high \( \text{pH} \) values provides the reason for the increasing As/Ga ratio of the oxide grown at lower \( \text{pH} \) environment. At low \( \text{pH} \) values, not only the polyoxycations but also the oxides are dissociated into the ionic gallic, i.e., etched by the solution, although the dissolution of As compounds are suppressed as compared to that in the solutions of higher \( \text{pH} \) values.

Conclusion

Effects of \( \text{pH} \) on the GaAs oxide growth kinetics by liquid-phase chemical-enhanced oxidation technique have been investigated. The
high initial oxidation rate near room temperature is attributed to the chemical enhancement of gallium polyoxycation in aqueous solution. Concerning the hydrolytic behaviors of the oxide components and the hydrolyzed gallium cation, it is clear that the pH value of oxidation solution plays an important role in the present oxidation method. Within an optimum window of initial pH values, it is found that the oxide films can be grown at the highest oxidation rate. Outside the window, the oxide growth will be significantly delayed or suppressed. The pH-controlled procedure is demonstrated to be effective for dominating both the oxidation rate and the refractive index of grown oxide films. In addition, the SIMS depth profiles indicate that the increased As/Ga ratio leads to the increased refractive index of the oxide film. Finally, the proposed model can be used to interpret the observed phenomena well.

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References