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Digital Etching of InP Using Tris-Dimethylaminophosphorus in Ultra-High Vacuum

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1. Introduction

Atomic layer epitaxy (ALE) [1,2] and molecular layer epitaxy (MLE) [3] are promising technology for fabricating very thin layers. Recently, the combination of an etching and a growth in an identical equipment has been emerging as a very promising technique for the surface cleaning and the fabrication of nanoscale structures, such as quantum dots [4]. However, in InP, it becomes much more difficult to obtain a clean surface, because the surface during thermal cleaning is too much sensitive to a slight inhomogeneity of the flux of phosphorus precursors, and because of the narrow temperature allowance of thermal cleaning. Therefore, low-temperature in-situ digital etching [5], in which etching depth is controlled not by injection time or injection pressure of etching gas but by the number of injection cycles, is strongly desired. Tris-dimethylamino-phosphorus (TDMAP) is known to be less toxic and is expected to be low carbon incorporation for growths [6]. However, precise control of etching with TDMAP has not been reported yet. In this paper, TDMAP is used for selective etching in an ultra-high vacuum MLE equipment. Low-temperature digital etching is successfully demonstrated at a substrate temperature as low as 350°C.

2. Experimental

The MLE chamber [7] is evacuated to a background pressure of around 1×10^{-9} Torr by a turbo-molecular pomp. (001) oriented InP substrate, which is partially covered by a silicon nitride film, is used for the selective etching. The substrate in the chamber is heated by a halogen lamp from the surface. TDMAP with a injection pressure (P_T) of 1×10^{-4} Torr in the chamber is introduced intermittently with an injection time (t_i) of 0.1 to 15 sec, an evacuation time (t_e) of 5 to 15 sec, and injection cycles (N) of 100 to 300. The substrate temperature (T_s) is 350 to 400°C. The etching depth is measured by a mechanical depth profiler after removing the silicon nitride film by HF solution.

3. Results and Discussion

The dependence of etching depth on injection cycle for different injection time of TDMAP is shown in Fig. 1. The etching depth proportionally increases with the number of injection cycles, that is independent of injection time. Therefore, etch rate defined as the etching depth per one injection cycle. The dependence of etch rate on injection time of TDMAP for different injection pressure and different substrate temperature is shown in Fig. 2. The etch rate is independent of injection time when the injection time is over 1 sec. Assuming a simple Langmuir-type adsorption of TDMAP without desorption and its exclusive contribution to etching, the dependence of etch rate (R_e) on injection time (t_i) is given by:

$$R_e = R_{sat}\,[1-\exp(-k_{eff}\,P_T\,t_i)] \qquad (1)$$

where R_{sat} is a saturation value and k_{eff} is an effective adsorption rate constant in relation to the partial pressure of supplied TDMAP, P_T [8]. The relation described by dotted lines in Fig. 2 is calculated by eq. (1) with an identical effective adsorption rate constant of 1.1×10^5 (Torr sec)$^{-1}$ for both injection pressures. The dependence of etch rate on injection pressure of TDMAP is shown in Fig. 3. The etch rate is almost independent of injection pressure. The etch rate is also almost independent of evacuation time. Therefore, digital etching is successfully demonstrated using TDMAP. Figure 4 shows the dependence of etch rate (R_e) on substrate temperature by open circles and the dependence of decomposition rate (R_d) per evacuation time on substrate temperature by closed circles. The decomposition rate is defined as the etching depth per evacuation time during continuous evacuation without TDMAP supply. It is assumed that the etching without TDMAP supply results from phosphorus decomposition. The activation energy for digital etching (1.27 eV) is smaller than that for phosphorus decomposition from InP surface without TDMAP supply (2.67 eV). Thus an stable digital etching is realized at a substrate temperature as low as 350°C.

4. Conclusions

The intermittent injection of TDMAP has been used for the selective etching of InP in the ultra-high vacuum MLE equipment. The etch rate was controlled with a self-limiting fashion and that was well described by the Langmuir-type equation. It is predicted that TDMAP is adsorbed on the InP surface within 1 sec and sticks during evacuation for more than 15 sec, and the decomposition of phosphorus from InP is suppressed at the substrate temperature lower than 400°C. Low-temperature digital etching is successfully demonstrated at a substrate temperature as low as 350°C, that results form it's low activation energy (1.27 eV).

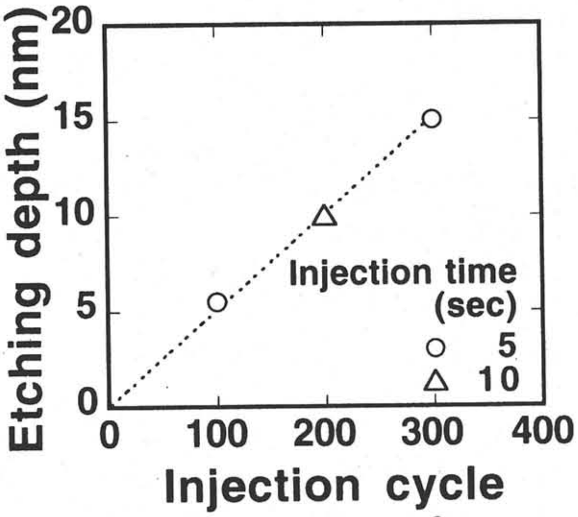

Fig. 1. Dependence of etching depth on injection cycle for different injection time of TDMAP. (t_e=5 sec, T_s=400°C, P_T=1×10^{-4} Torr)

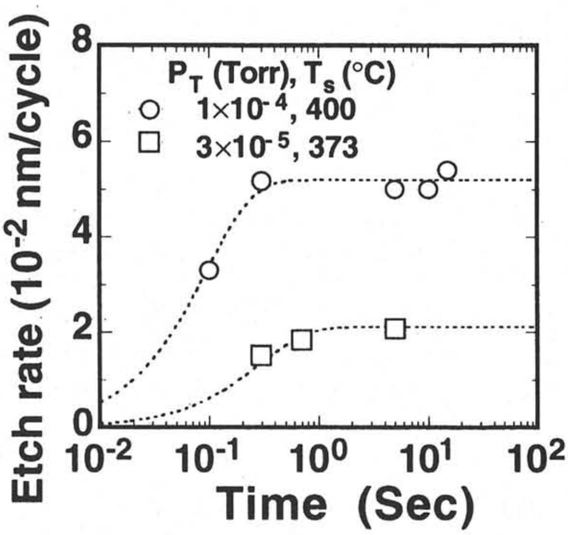

Fig. 2. Dependence of etch rate on injection time of TDMAP for different injection pressure (P_T) and different substrate temperature (T_s). (t_e=5 sec, N=300)

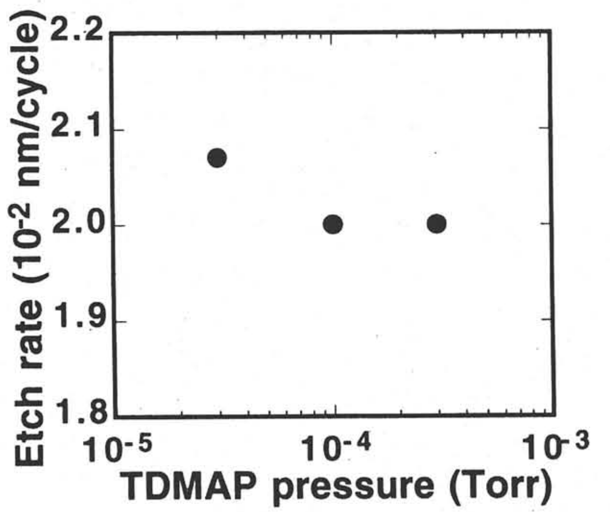

Fig. 3. Dependence of etch rate on injection pressure of TDMAP. (t_l=t_e=5 sec, T_s=400°C, P_T=1×10^{-4} Torr, N=300)

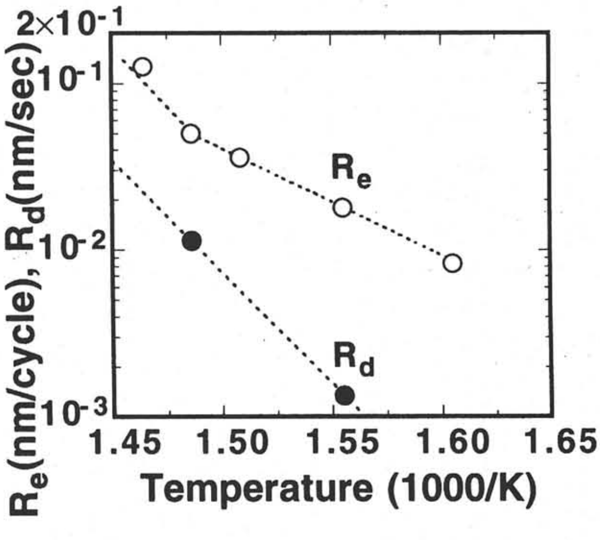

Fig. 4. Dependence of etch rate on substrate temperature (○, t_l=t_e=5 sec, P_T=1×10^{-4} Torr, N=300). Dependence of decomposition rate of phosphorus per evacuation time (●).

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