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Selective wet etching of $Al_{0.7}Ga_{0.3}As$ layer in concentrated HCl solution for peeling off GaAs microtips

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ABSTRACT

Selective wet etching of an $Al_{0.7}Ga_{0.3}As$ sacrificial layer, sandwiched between two GaAs layers, at different HCl concentrations and temperatures has been investigated. This technique can be used in peeling off GaAs microtips for scanning near-field optical microscopy. The results show that the etching rate remains almost constant in a large range of etching length for the concentrated HCl etching of $Al_{0.7}Ga_{0.3}As$ at a certain temperature. However, the etching rates increase very quickly for both $Al_{0.7}Ga_{0.3}As$ and GaAs as the etching temperature increasing. Furthermore, the concentrated HCl at 0 °C is the optimal condition for selective wet etching of $Al_{0.7}Ga_{0.3}As$, at which the etching rate is about 0.5 μm/min for $Al_{0.7}Ga_{0.3}As$, but close to 0 μm/min for GaAs. Finally, the GaAs microtip, grown on the $GaAs/Al_{0.7}Ga_{0.3}As/GaAs$ sandwich structure, is peeled off by concentrated HCl selective etching of $Al_{0.7}Ga_{0.3}As$ layer at 0 °C. Scanning electron microscopy image demonstrates that the GaAs microtip can be successfully removed without damage by the above-mentioned method.

1. Introduction

A reproducible selective wet etching is important to the processing of the devices based on $GaAs/Al_xGa_{1-x}As$ such as semiconductor laser [1], field effect transistor [2] and optical waveguide [3]. It also has an important application in peeling off GaAs microtips for producing integrated scanning near-field optical microscopy (SNOM) sensor, which has become one of the most promising candidates for future ultrahigh-density data storage. Gorecki et al. has proposed a configuration of integrated SNOM sensor composed by a GaAs microtip, a vertical-cavity surface-emitting laser (VCSEL) cavity and a PIN (p-AlGaAs/i-GaAs/n-AlGaAs) monitor [4]. At present, many techniques are quite mature for manufacturing VCSEL cavity with a PIN monitor and also some techniques [5–8] have been developed to fabricate GaAs microtips on GaAs substrates. Considering the process compatibility problem, it is still difficult to directly grow GaAs microtips on the emitting window areas of a VCSEL wafer to form monolithic integrated SNOM sensor structures. Thus, transferring GaAs microtips onto a VCSEL wafer to realize a hybrid integrated SNOM sensor becomes a practical approach. In order to transfer the GaAs microtips grown on an independent substrate onto a target wafer, it is indispensable to remove the GaAs microtips from the substrate. For this purpose, we develop a simple and reproducible GaAs microtips peeling technique based on growing GaAs microtips on $GaAs/Al_xGa_{1-x}As/GaAs$ sandwich structure and then selective etching of the $Al_xGa_{1-x}As$ layer.

Conventionally, for the wet etching of the AlGaAs sacrificial layer, an etching solution based on HF acid has been used due to the large etching selectivity of approximately 10^7 between AlAs and GaAs [9–12]. However, it has been suggested that H_2 bubbles generated in the reaction zone hinder the etching process by displacing the etchants, and damage the fragile device structure due to the hydrostatic pressure caused by their formation during the etching process [10]. While recent report indicates that H_2 is not the major reaction product, other gas-phase products, such as AsH_3 resulting from the etching process and a low solubility-etching product (AlF_3), which has also been implicated as a potential etch hindering compound [13]. In addition, the HCl-based solution has been qualitatively proven to have a larger etching selectivity between the AlAs and $Al_{0.1}Ga_{0.9}As$ layers and less damage to the suspended structure [14]. Therefore, in this study, the HCl-based solution rather than a HF-based one was employed as the solution for selective wet etching the high Al composition $Al_xGa_{1-x}As$ layer with the x of 0.7. Etch-blocking behavior wasn't observed even when using concentrated HCl as the etchant and the GaAs microtip was successfully peeled off from the independent GaAs substrate by HCl-based solution. Meanwhile, the etching rates of both $Al_{0.7}Ga_{0.3}As$ and GaAs under different HCl concentrations and temperatures were also studied.

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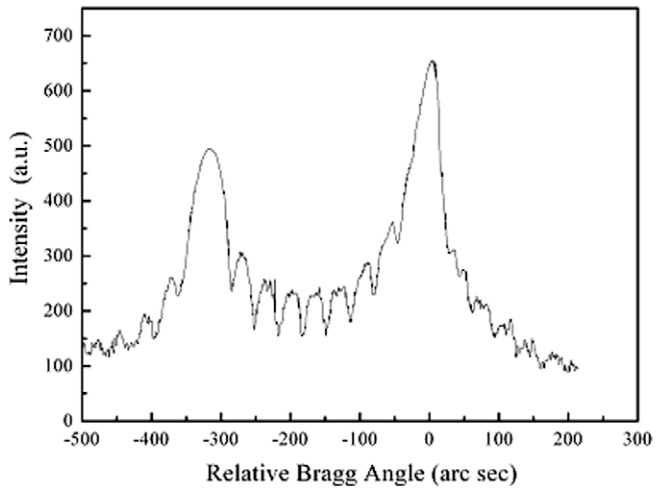

Fig. 1. The DCXRD profile of the GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs sandwich structure for (0 0 4) plane.

2. Experiment

Prior to fabricating GaAs microtips, an optimizing experiment for etching conditions was conducted as follows: an $Al_{0.7}Ga_{0.3}As$ layer and a GaAs layer were firstly grown on GaAs (0 0 1) substrate by MOCVD in turn to form a GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs sandwich structure. The GaAs epitaxial layer was for growing GaAs microtips. The thicknesses of the $Al_{0.7}Ga_{0.3}As$ and GaAs layers were about 1 μm and 0.5 μm, respectively. Then, the wafer was patterned with standard photolithography to form periodic stripe windows of 10 μm width orienting parallel to the ⟨0 1 1⟩ directions. Before patterned, the wafer was cleaned by toluene, acetone and absolute alcohol in turn, followed by deionized rinse. Next, the wafer was immerged in a 188 solution (H_2SO_4:H_2O_2:H_2O = 1:8:8) at 0 °C for 35 s to completely etch away the GaAs and $Al_{0.7}Ga_{0.3}As$ epitaxial layers in the stripe windows for the lateral selective etching of $Al_{0.7}Ga_{0.3}As$ layer. In order to avoid the residual of the GaAs epitaxial layer, the partial GaAs substrate in the windows was also etched away. The total etching depth was about 6 μm. And then the test structure was divide into several parts to obtain their lateral etch characteristics at different HCl concentrations and temperatures. The HCl solution was prepared according to a volume ratio of 2:1, 1:1 with DI water and a concentrated HCl solution (37%) was also prepared. For each volume ratio, the wafer was submerged in the HCl solution at different temperatures of 0 °C, 30 °C and 60 °C to carry out the lateral selective etching of $Al_{0.7}Ga_{0.3}As$ layer. In the whole experiment process, a temperature-controlled container of etchant was used for the study of temperature effects and no agitation was done during the etching process. The etching process was stopped by rinsing the samples in deionized water, followed by blowing dry with nitrogen. The lateral etching length of the $Al_{0.7}Ga_{0.3}As$ sacrificial layer as a function of etching time was observed by metallurgical microscopy (BX51 M, OLYMBUS). And the Al composition of the $Al_{0.7}Ga_{0.3}As$ layer was determined according to double-crystal X-ray diffraction (DCXRD) measurement (SLX-1A, Rigaku).

Based on the above optimizing experiment, the optimal condition for selective wet etching of $Al_{0.7}Ga_{0.3}As$ was obtained. Then the GaAs microtips array was grown on another GaAs substrate with GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs sandwich structure by selective LPE [8]. Finally the GaAs microtips were removed from the substrate using the method of HCl selective wet etching of $Al_{0.7}Ga_{0.3}As$ sacrificial layer mentioned above. Scanning electron Microscopy (SEM, JEOL-JSM 6500F) was employed to characterize the configurations of the removed microtips.

3. Results and discussion

Fig. 1 shows the DCXRD profile of the (0 0 4) reflection of the GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs sandwich structure. From Fig. 1, the difference of Bragg reflection angle between the GaAs and AlGaAs layers is about 308″, thus the Al composition of the AlGaAs layer is calculated about 0.7 by Vegard's Law.

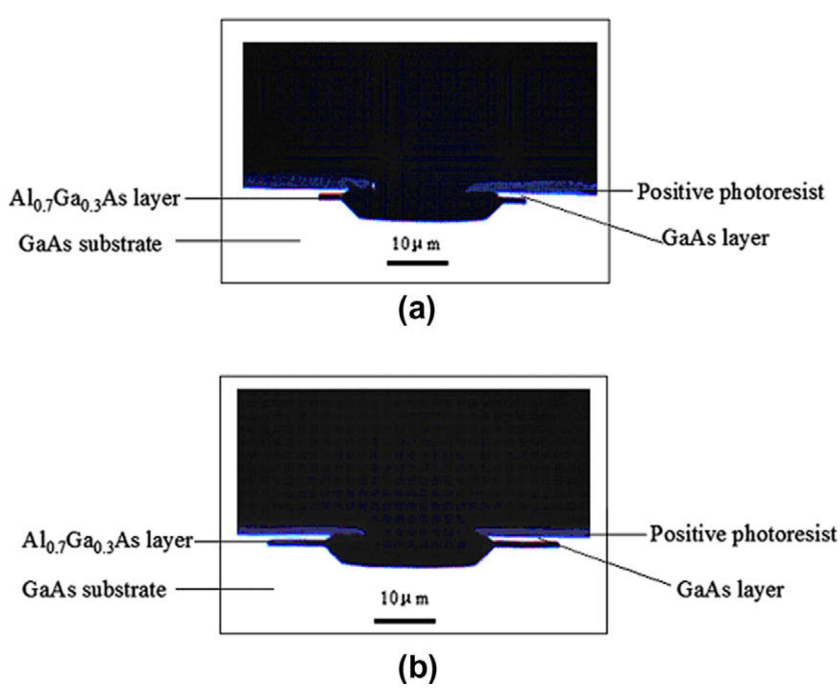

Fig. 2. The cross-sectional images of the sandwich structure etched by a 188 solution for 35 s and then etched by a concentrated HCl etchant at 0 °C, (a) for 6 min and (b) for 15 min.

Fig. 2 shows the metallurgical microscopy cross-sectional images of a GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs sample etched in turn by the 188 solution for 35 s at 0 °C and by the concentrated HCl solution at 0 °C for 6 min (a) and 15 min (b). According to Fig. 2, the shape of the groove formed in the stripe window is reversed ladder-like after etched by the 188 solution, and the lateral selective etching depths of the $Al_{0.7}Ga_{0.3}As$ layer are about 3 μm for the etching of 6 min and 8 μm for the etching of 15 min, respectively. Moreover, according to Fig. 2a and b, the depths of the two grooves are almost same, which indicates that the concentrated HCl solution is no erosion for GaAs at 0 °C during the etching process and the concentrated HCl solution has a good selective etching specialty for the $Al_{0.7}Ga_{0.3}As$ layer.

Fig. 3 plots the lateral etching lengths of $Al_{0.7}Ga_{0.3}As$ and GaAs layers as functions of etching time by different HCl concentrations at 0 °C. The lateral etching length of $Al_{0.7}Ga_{0.3}As$ is over 100 μm for this test. During the etching process, GaAs is not eroded for all the different concentration HCl solutions at 0 °C, shown in Fig. 3a. For $Al_{0.7}Ga_{0.3}As$ layer, when the lateral etching length is linear with etching time, etch-blocking behavior is not observed and the etch rate is about 0.5 μm/min for the concentrated HCl solution as the etchant, shown in Fig. 3d. While the etching process is limited by 35 μm for the volume ratio of 2:1 HCl solution, shown in Fig. 3c and no obvious etching process is observed for the volume ratio of 1:1 HCl solution at 0 °C, shown in Fig. 3b. The termination of etching $Al_xGa_{1-x}As$ for the volume ratio of 2:1 and 1:1 HCl solution maybe due to the HCl being so dilute that the etching process is limited by the reaction at the etching front. So far, the detailed reaction mechanism of $Al_xGa_{1-x}As$ etched by HCl is unknown. It is assumed that AsH_3, $AlCl_3$, and $GaCl_3$ are the major reaction products in the etching process of $Al_xGa_{1-x}As$ etched by HCl, similar to HCl etching of InP. It has been proved that all the three major products in the process of HCl etching of $Al_xGa_{1-x}As$ will rapidly hydrolyze and dissolve. As a result, the products easily diffuse away from shallow etch channels and no etch-blocking behavior is observed for the concentrated HCl selective wet etching of $Al_{0.7}Ga_{0.3}As$ at 0 °C. Compared with HF etching of $Al_xGa_{1-x}As$, it has been reported that AlF_3 is formed during this case and it has also been reported that the AlF_3 product is only sparingly soluble [15]. Therefore, the formation of the insoluble trifluoride, which may be in the hydrated form, can explain the termination observed in HF system etching of $Al_xGa_{1-x}As$. In addition, it has been reported that HCl-based solution has less damage than HF-based one for selective wet etching of AlGaAs because the solubility of the byproduct gas in the HCl-based solution is higher than that of the byproduct gas in the HF-based one [14].

Fig. 4 exhibits the lateral etching lengths of $Al_{0.7}Ga_{0.3}As$ and GaAs layers as functions of etching time by concentrated HCl at different temperatures. It is seen that for the $Al_{0.7}Ga_{0.3}As$, the etching rates at temperatures below 60 °C remain almost constant throughout the entire process at each centigrade degree but presents enhancing as the temperature increasing. At the same etching length of 30 μm, the variation of the lateral etching rates is about 0.5 μm/min for 0 °C and 2.5 μm/min for 60 °C. It is indicated that the etch time will be reduced by increasing the temperature for a certain lateral etching length. However, it should be noted that concentrated HCl has stronger influence on the etching of GaAs as the temperature increasing, which may damage the GaAs epitaxial layer and even the GaAs microtips. Therefore, it can be

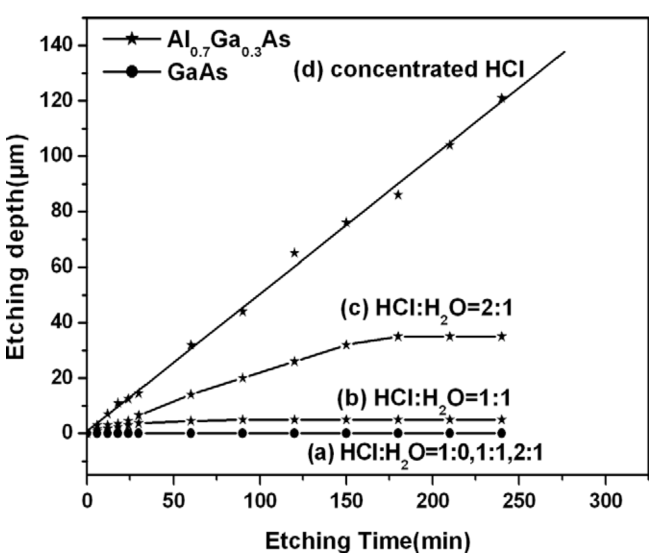

Fig. 3. The dependences of the etching depth on etching time for $Al_{0.7}Ga_{0.3}As$ and GaAs by different HCl concentrations at 0 °C, (a) $HCl:H_2O = 1:0$, 1:1, 2:1 etching of GaAs, (b) $HCl:H_2O = 1:1$ etching of $Al_{0.7}Ga_{0.3}As$, (c) $HCl:H_2O = 2:1$ etching of $Al_{0.7}Ga_{0.3}As$ and (d) concentrated HCl etching of $Al_{0.7}Ga_{0.3}As$.

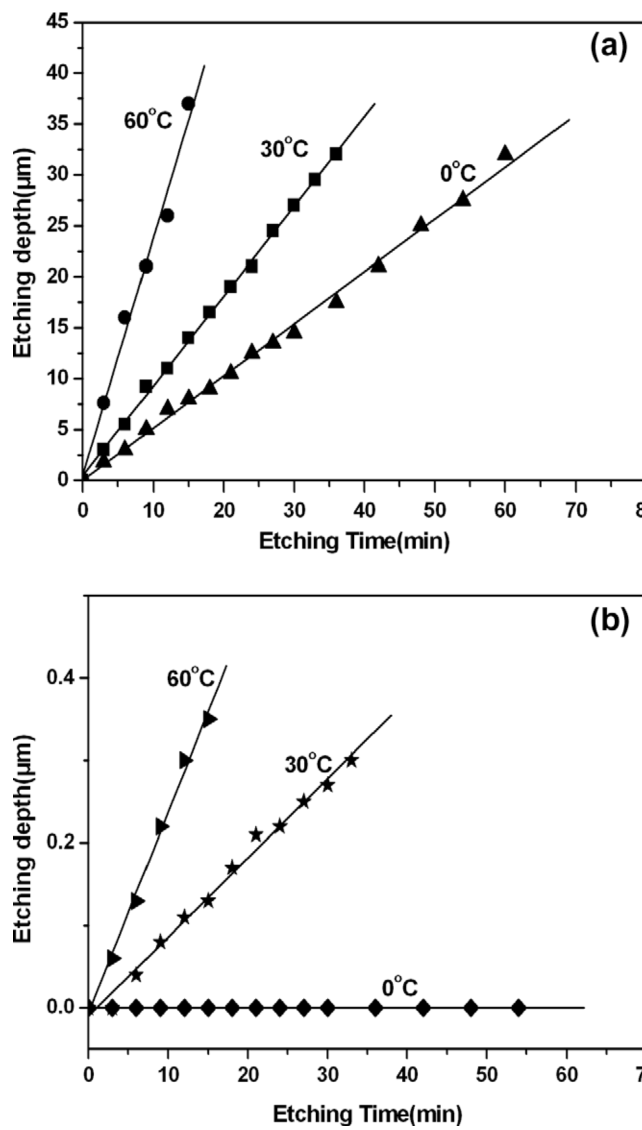

Fig. 4. The dependences of the etching depth on etching time for $Al_{0.7}Ga_{0.3}As$ and GaAs by concentrated HCl at different temperatures.

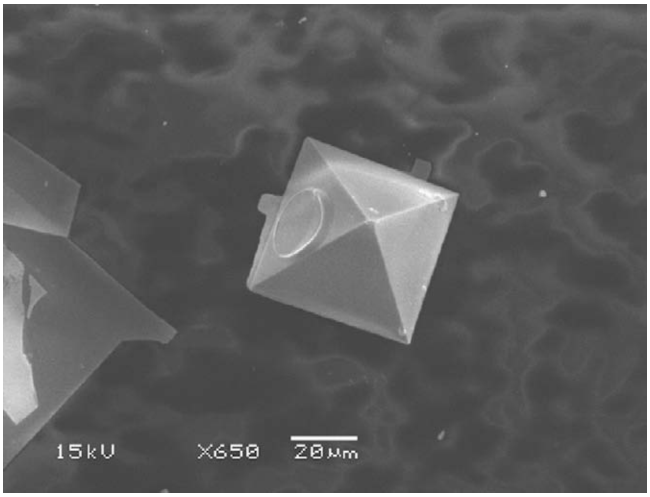

Fig. 5. A SEM image of a removed GaAs microtip.

deduced that the higher temperature results in higher etching rate of $Al_{0.7}Ga_{0.3}As$ sacrificial layer, while it may also reduce the selectivity, and as well make it more difficult to accurately control the etching process and even damage the GaAs microtips. So concentrated HCl etching of $Al_{0.7}Ga_{0.3}As$ at 0 °C is considered to be the optimal condition for peeling off GaAs microtips, at which the etching rate is about 0.5 μm/min for $Al_{0.7}Ga_{0.3}As$ and nearly no influence on GaAs.

Prior to the GaAs tip removed from the GaAs substrate by the above-mentioned method, a positive photoresist layer with a thickness over 100 μm is spun to embed and protect the tip. Then the peeling off GaAs tip is bonded on a Si wafer by negative photoresist and finally the positive photoresist is removed in acetone. Fig. 5 shows the SEM image of a GaAs microtip peeled off by the selective etching $Al_{0.7}Ga_{0.3}As$ layer using concentrated HCl at 0 °C. It is observed that the GaAs microtip still keeps in a sharp point apex bounded by four {1 1 1} sidewalls (two {1 1 1} A and two {1 1 1} B planes) and the {1 1 1} sidewalls of the pyramid are extremely smooth and flat except the left one on which a large spot, resulting from the residual melt after growth. Neither the top nor the sidewalls are attacked during the selective wet etching process indicating that the removed GaAs tip keeps in a high quality. Therefore, it can be concluded that the concentrated HCl etching of $Al_{0.7}Ga_{0.3}As$ sandwiched between GaAs layers is suitable to peel off GaAs microtip with the perfect selectivity and less damage.

4. Conclusions

We have demonstrated the experiment results of the selective etching of an $Al_{0.7}Ga_{0.3}As$ layer sandwiched between two GaAs layers with HCl-based solution. The dependences of the lateral etching rates of the $Al_{0.7}Ga_{0.3}As$ sacrificial layer on the HCl concentrations and temperatures have been investigated. No etch-blocking behavior is occurred using concentrated HCl as etching solution at 0 °C, while the etching termination is happened for the dilute HCl solution. The etching rate is independent of the etching length but is affected strongly by the temperature. The concentrated HCl at 0 °C is the optimal condition for selective etching of $Al_{0.7}Ga_{0.3}As$ to remove GaAs tips. The SEM image demonstrates that the GaAs microtip is successfully removed from GaAs/$Al_{0.7}Ga_{0.3}As$/GaAs structure to the target wafer without damage by selective etching of $Al_{0.7}Ga_{0.3}As$ layer using concentrated HCl at 0 °C. The results further show that the simple and reproducible selective etching technique can be applied for peeling and transferring of the GaAs microtip grown on the GaAs layer, which is a promising technique to realize a hybrid integrated scanning near-field optical microscopy sensor.

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