25 nm pitch GaInAs/InP buried structure: Improvement by calixarene as an electron beam resist and tertiarybutylphosphine as a P source in organometallic vapor phase epitaxy regrowth

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To achieve a fine periodic semiconductor structure by electron beam (EB) lithography, calixarene was used as an EB resist. A 25 nm pitch InP pattern was formed successfully and 40 nm pitch InP structures were achieved with good reproducibility. A shorter developing time, precise stage motion, accurate control of the widths of lines and spaces, and slight O_2 ashing were important to obtain a fine InP pattern by a two-step wet chemical etching process. Furthermore, the fabricated periodic InP pattern was buried in a GaInAs structure by organometallic vapor phase epitaxy. The introduction of tertiarybutylphosphine as the phosphorus source prevented the fine structure from deforming when the temperature was raised and a 25 nm pitch periodic structure was buried successfully. © *1998 American Vacuum Society.* [S0734-211X(98)09306-8]

I. INTRODUCTION

Quantum mechanics will provide an attractive principle for new devices when the period of lateral patterns is comparable with the electron wavelength.[1] One of the most powerful tools for fabricating such a fine structure is electron beam lithography (EBL). To confirm the wave nature of electrons in semiconductors, we earlier proposed Young's double slit experiment in semiconductors using a lateral structure fabricated by EBL[2] and reported a 40 nm pitch GaInAs/InP double slit structure by poly(methylmethacrylate) as the resist.[3] However, the reproducibility of the structure with a 40 nm period was very low and we could not fabricate a structure finer than 40 nm.

Recently, a semiconductor pattern with a 7 nm width was reported by using calixarene as the EB resist.[4] However, there is no report on the fabrication of a fine period pattern using calixarene resist.
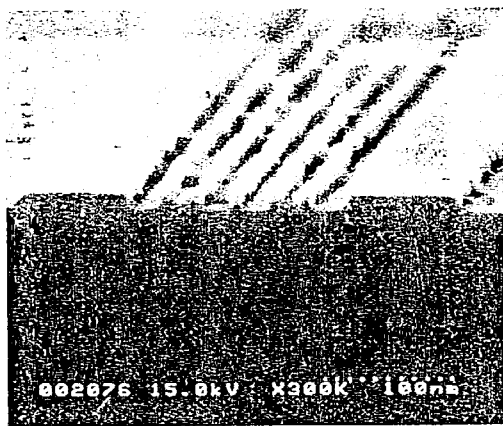
In this article, we describe the fabrication of a fine periodic InP structure. We fabricated a 25 nm pitch InP pattern by using a calixarene resist. The ultrahigh resolution of calixarene improved the reproducibility of a 40 nm periodic pattern. A regrowth process by organometallic vapor phase epitaxy (OMVPE) is also reported to bury InP fine structures in GaInAs. By the introduction of tertiarybutylphosphine (TBP) as the phosphorus source, the deformation of these fine structures was prevented and a 25 nm pitch periodic structure was buried successfully.

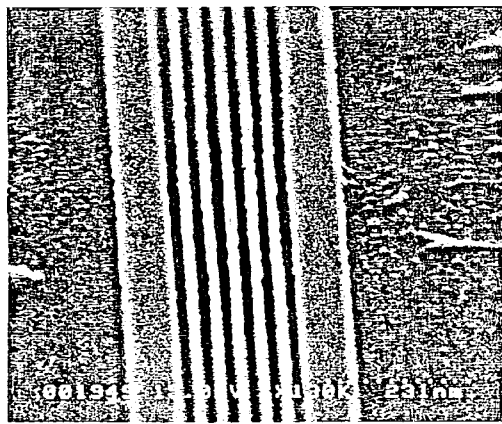## II. FABRICATION OF InP FINE PERIODIC PATTERN

A fine InP periodic pattern was formed by two-step wet chemical etching.[5] At first, an epitaxial structure with a 50 nm thick GaInAs layer, a 10 nm thick InP layer, and a 4 nm thick GaInAs layer was grown on a (100) n-InP substrate. Then, a resist pattern was formed by EB exposure using calixarene resist. The thickness of the resist was 17 nm. The conditions of EBL were 50 keV, 5 nm, and 0.62 nm as the accelerating voltage, nominal spot size, and nominal accuracy for beam positioning using a precise laser interferometer and electronic position feedback in combination with a very stable mechanical table, respectively.

Fine periodic patterns with 20, 25, 30, and 40 nm periods were exposed. All of the patterns consisted of five lines to fabricate the slit structure and 150 nm wide rectangles on both sides to protect the slit layer. The dose to expose the lines with a 25 nm period was 32 nC/cm. Development was carried out by dipping in xylene for 30 s followed by rinsing in isopropyl alcohol for 30 s. After the formation of the resist patterns, slight O_2 ashing was carried out followed by a first wet etching of a 4 nm thick GaInAs layer by a citric acid: $H_2O:H_2O_2 = 20:50:1$ solution. The etching time was 6 s and the etching rate of GaInAs with this solution was 0.7 nm/s. The etching time was selected for minimized undercut etching, since we did not observe etching of InP with this solution. Then, the resist was removed by O_2 ashing and the pattern was transferred from the GaInAs layer into a 10 nm thick InP layer by a second wet etching step using a $HCl:CH_3COOH = 1:4$ solution. The etching time was 30 s and the etching rate of InP with this solution was 22 nm/s.

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(a)

(b)

FIG. 1. SEM photograph of an InP grating: (a) A 25 nm pitch pattern with cleaved facets. Cross section shows a rectangular shape of InP rectangles. (b) Top view of a SEM photograph of a 40 nm pitch InP grating. No bridge was observed: observation was carried out from 70° to normal to observe a wider region in the direction of the lines and magnification of the depth side was reduced by a factor of 3. Please note that the bar for the length had a 10% – 15% error due to the limitation of our SEM.

Since the etching of InP stops automatically by material selectivity between GaInAs and InP and anisotropy to the facet,[5] the etching time was much longer than required from the etching rate.

Figure 1(a) shows a 25 nm pitch InP pattern imaged in a scanning electron microscope (SEM). A rectangular InP profile can be observed.

In the formation of the resist pattern, swelling of the resist and stage motion of EBL[6] caused deformation. A resist pattern of ten lines with a 25 nm period [shown in Fig. 2(a)] was exposed by EBL whose nominal accuracy for stage motion was 5 nm, and was developed in xylene for 70 s. Wavy ridge lines and lines sticking together can be observed in Fig. 2(a). These wavy ridge lines are due to insufficient control of the stage motion in a long exposure time for the high dose requirements of calixarene and a low current beam.

When Fig. 2(a) was viewed from a shallow angle, three periods of parallel waves could be observed on the left hand side. The observed period and amplitude were 490 and 3 nm.

The period of the parallel wave corresponded to 85 Hz, although a different frequency was observed in another experiment (140 Hz). We could not speculate on the reason for this parallel stage motion exactly, but we could confirm that the ridge lines became straight, as shown in Fig. 2(b), when the accuracy of the stage motion was improved by the improvement of the laser interferometer (the resolution of the measurement became wavelength/1024 from wavelength/128) while the other conditions remained the same.

The dependence on the developing time was also confirmed by a change in the time when other conditions remained the same. We confirmed that the developing time of 70 s caused swelling and waving in the resist patterns. A longer developing time offers the possibility of providing higher resolution in a negative resist. But because a developing time of 70 s caused swelling as shown in Fig. 2(b), we reduced the developing time to 30 s and a reduction in the swelling was observed as shown in Fig. 2(c).

Slight O_2 ashing just before wet etching is effective in removing residue between lines. In observations using SEM, we could not find anything between lines just after development and no shape changes were observed after slight O_2 ashing. However, the slight O_2 ashing was found to be effective in reducing bridges after transferring patterns. The amount of etching was around a few nanometers.

In transferring patterns into InP,[5] the anisotropic nature of etching is used and the lines must be parallel to the (011) direction for rectangular facet etching.[7] Since a flat (01$\bar{1}$) side facet of the etched groove is generated by a high etching rate in the lateral direction, wavy lines become narrower than the width of resist lines after the InP etching. These narrow lines have the possibility of falling over during drying from a wet solution and are easily deformed by raising the temperature during regrowth as will be mentioned later. On the other hand, lines sticking together by swelling create bridges between each other and these bridges result in trapezoidal structures with (11$\bar{1}$)B etch-stop facets[7] under the bridges. Therefore, the widths of lines and spaces must be designed carefully to fabricate fine periodical structures.

At present, the range for the line dose is not wide enough to fabricate periodical structures with a 25 or 30 nm pitch. The linewidth must be controlled by the line dose to avoid the falling of high aspect ratio lines and to avoid the creation of bridges over narrow spaces. However, an InP pattern without bridges in a large area was not reproducible under the present conditions.

Patterns with a 40 nm period were exposed by a single line scan in the early stages of the experiment. However, the width of the obtained InP lines became narrower than the spacing. This was due to the high resolution of calixarene. Then, a rectangular exposure was carried out to obtain etched lines of a stable width. A SEM photograph of the surface of a 40 nm pitch InP structure is shown in Fig. 1(b). Lines of 20 nm width were exposed with a dose of 20 mC/cm². In the case of 40 nm pitch periodical structures, because the exposure conditions are not so critical, we could reproduce patterns without bridges.
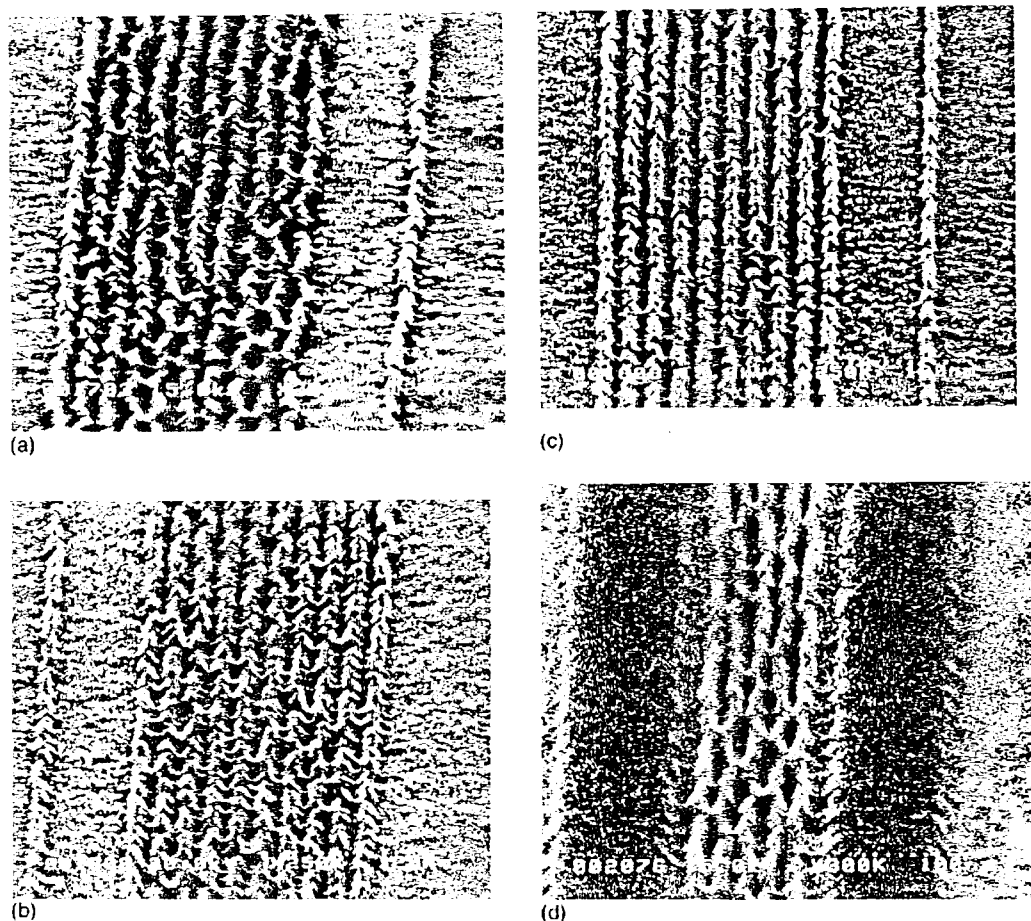
FIG. 2. Resist patterns observed by SEM. Observation was carried out from 70° to normal to observe a wider region in the direction of the lines. (a) Pattern in the former experiment consisting of ten lines with a 25 nm period. Differences from the present experiment are a poorer accuracy of stage motion and a longer developing time. (b) Pattern after improvement of the accuracy for the stage motion which improved from 5 to 0.62 nm. (c) Pattern after reduction of the developing time which was reduced from 70 to 30 s. (d) Pattern with a 20 nm period.

For 20 nm period patterns at present, no periodical InP pattern can be formed. A typical resist surface after development is shown in Fig. 2(d). The ridge lines are wavy although as shown Fig. 2(c), the ridge lines of 25 nm pitch periodical structures obtained under the same conditions were straight. We consider that deformation by swelling defeats adhesion between the resist and the surface and causes the sticking together. Since the transferring of patterns by wet chemical etching does not require a thick resist because of the high selectivity in the etching, the reduction of the resist thickness can be effective in preventing deformation of the resist because a thinner resist causes less swelling with the same adhesion to the surface.

III. BURIED GROWTH BY OMVPE

For Young's double slit experiment in semiconductors,[2] buried slits in the semiconductors are required. To apply an InP grating to the buried slits, the sample is embedded in regrown GaInAs by OMVPE. In the regrowth, the deformation of fine structures must be prevented. When the partial pressure of phosphorus is low while increasing the tempera-

ture to the growth temperature, indium from the InP fine structure can move easily on the surface (the so-called "mass transport") resulting in deformation of the fine structure.

To prevent the deformation, PH_3 and AsH_3 were introduced at high flow rates to get a high partial pressure of V groups and the starting temperature of regrowth was selected to be as low as possible in the former experiment.[8] The fabricated InP structure was buried under previously reported conditions.[8] Raising the temperature was started with the introduction of PH_3 and AsH_3. The partial pressures of PH_3 and AsH_3 were 1.65 and 0.81 Torr, respectively. When the temperature reached 550 °C, the flow of PH_3 was stopped and the growth of a 10 nm thick GaInAs layer was started by the introduction of triethlygallium (TEG) and trimethylindium (TMI). The temperature was changed from 550 to 590 °C when the GaInAs layer was grown and the growth was interrupted until the temperature became stable at 600 °C. After the stabilization, a 150 nm thick GaInAs layer and a 10 nm thick InP layer were grown.

In the case of the grating with a 40 nm period, we could observe a buried periodical structure as shown in Fig. 3(a),
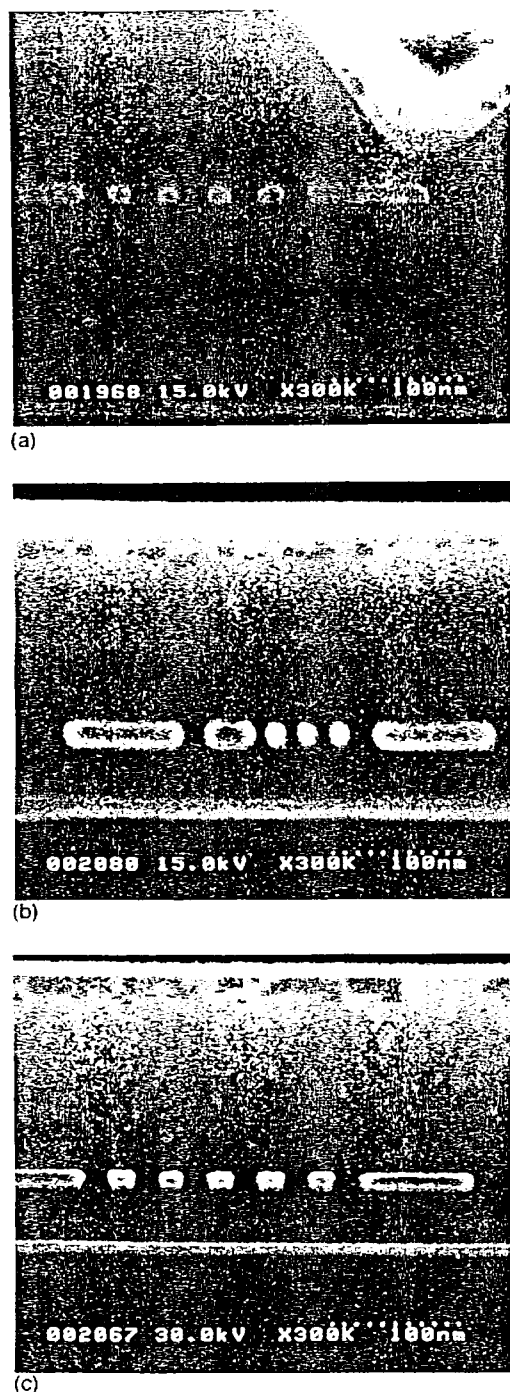
(a)

(b)

(c)

FIG. 3. Cross-sectional view of GaInAs/InP buried grating structure by SEM. Bright part is InP while the dark part is GaInAs: (a) 40 nm pitch buried structure regrown without TBP, (b) 25 nm pitch buried structure regrown with TBP, (c) 40 nm pitch buried structure regrown with TBP.

although the edges of the rectangular cross sections were rounded. However, we could hardly find a buried grating having a periodical structure with a 25 nm pitch. The observed buried InP rectangles with a 25 nm period were deformed completely and appeared as small blurry spots in a cross-sectional SEM image. The size of the spots was reduced from the original height by more than a factor of 2.

The problem of deformation became more severe when InP structures were reduced with a finer pitch by using calixarene. The insufficient partial pressure of phosphorus in the former experiment was due to the low decomposition rate of PH_3 in the range of the raised temperature employed (400–500 °C). Therefore, we introduced a TBP supplying system in a newly designed OMVPE process because the decomposition temperature of TBP is lower than that of PH_3.[9] There is also the possibility that TBP enhances the decomposition of PH_3.[9]

The conditions for regrowth with TBP were as follows. When the temperature was raised, TBP was introduced with PH_3 and AsH_3. The partial pressures of TBP, PH_3, and AsH_3 were 0.76, 2.28, and 0.76 Torr, respectively. When the temperature was raised to 540 °C, TBP and PH_3 were exchanged for TEG and TMI to grow a 10 nm thick GaInAs layer. When the temperature was 590 °C, the growth was interrupted until the temperature stabilized at 650 °C. After the stabilization, a GaInAs layer and a InP layer were grown.

A cross-sectional view of buried 25 nm pitch periodical structures is shown in Fig. 3(b). Three periodical InP rectangles were confirmed although the fourth and fifth InP rectangles merged. The height of the periodical rectangles was almost the same as that of the rectangles on both sides. The merger of the rectangles on the left side was caused by the bridge in the resist.

In the case of a 25 nm period, the control of the width of the rectangles is not as easy as mentioned before and the unstable width of the rectangles makes it difficult to evaluate any deformation because the width of the InP rectangles affects the degradation in the regrowth. To confirm less deformation in regrowth with TBP, wider InP rectangles with a 40 nm period were buried. A cross-sectional view of buried 40 nm pitch InP structures is shown in Fig. 3(c). Although the size of the structures was close to the resolution limit of the SEM and selective wet etching for SEM observation may degrade the shape, we confirmed less deformation of the edges and straighter lines in the side facets than those shown in Fig. 3(a).

IV. CONCLUSIONS

A 25 nm pitch resist pattern transferable to InP layers was fabricated by using calixarene as the EB resist. The reproducibility of a 40 nm pitch pattern was improved by using calixarene. Using a shorter developing time, precise stage motion, slight O_2 ashing, and accurate control for the widths of lines and spaces were important in obtaining a fine InP pattern.

A fabricated fine InP grating was buried in GaInAs to observe the wave nature of electrons from diffraction effects. TBP was introduced to prevent the deformation of the InP fine structure which is caused when the temperature is raised. As a result, a 25 nm pitch periodical buried structure was confirmed. Less deformation of a 40 nm pitch periodical structure showed the effect of TBP.

ACKNOWLEDGMENTS

[1] K. Furuya, J. Appl. Phys. 62, 1492 (1987).

[2] H. Hongo, Y. Miyamoto, J. Suzuki, M. Funayama, T. Morita, and K. Furuya, Jpn. J. Appl. Phys., Part 1 33, 925 (1994).

[3] H. Hongo, Y. Miyamoto, J. Suzuki, T. Hattori, A. Kokubo, M. Suhara, and K. Furuya, Jpn. J. Appl. Phys., Part 1 37, 1518 (1998).

[4] J. Fujita, Y. Ohnishi, Y. Ochiai, and S. Matsui, Appl. Phys. Lett. 68, 1297 (1996).

[5] E. Inamura, Y. Miyamoto, S. Tamura, T. Takasugi, and K. Furuya, Jpn. J. Appl. Phys., Part 1 28, 2193 (1989).

[6] J. Fujita, Y. Ohnishi, Y. Ochiai, S. Manako, E. Nomura, and S. Matsui, Annual Meeting of Japan Society of Applied Physics, October 1996, paper 9a-S-4.

[7] L. A. Coldren, K. Furuya, B. I. Miller, and J. A. Rentschler, Electron. Lett. 18, 235 (1982).

[8] M. Suhara, Y. Miyamoto, H. Hongo, J. Suzuki, and K. Furuya, J. Cryst. Growth 145, 698 (1994).

[9] J. Komeno, J. Cryst. Growth 145, 468 (1994).