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High-temperature phosphorous passivation of Si surface for improved heteroepitaxial growth of InAs as an initial step of III-As MOVPE on Si

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1. Introduction

Most recently, conventional Si large scale integrated circuits (LSIs) greatly require III-V compound semiconductors for the channel layer of transistors and light source to enhance their performance itself or improve new functions. For this integration of III-V semiconductors on Si, we have proposed micro-channel selective-area growth (MC-SAG) [1] to overcome huge difference in lattice constants, and InGaAs growth has been studied using metal-organic vapor phase epitaxy (MOVPE). However, not InGaAs but InAs is suitable for obtaining a single nucleus and thus we have devised the multi-step growth in which the growth is started by InAs [2].

One of the most fundamental problems of heteroepitaxy of a III-V layer on Si is surface pretreatment: native oxide on Si has been removed and the clean Si surface will have to be stabilized by group-III atoms to promote initial nucleation of a III-V layer on Si. Moreover, in the case of MOVPE, the surface has to be protected from contamination inside a reactor. We have found that phosphorous treatment of Si, rather than arsenic, in an MOVPE reactor at the growth temperature is effective to promote uniform InAs nucleation on Si [3]. However, we have not yet achieved complete coverage of a Si growth area with an InAs flat island, which is desired to promote succeeding single-grain InGaAs growth with high uniformity. In this study, we tried higher pretreatment temperature than the growth temperature of 610°C, aiming at complete removal of silicon native oxide and perfect surface passivation with group-V atoms. Superiority P over As, or pure H_2, as an ambient of high-temperature pretreatment step has been confirmed. As a result, almost complete filling of a Si growth area with an InAs flat island has been achieved.

2. Experimental setup

We used Si(111) substrates without any patterns for investigating the surface contamination while patterned substrates were used for InAs growth. We treated the substrates chemically by a mixture of H_2SO_4 and H_2O_2 followed by diluted HF solution just before transfer into an MOVPE reactor. They were annealed in a horizontal single-wafer MOVPE reactor (AIXTRON, AIX200/4) at 850°C and at a total pressure of 10 kPa, with a total flow rate of 13 standard liters per minute with H_2 as the carrier gas. In the case of InAs growth, the temperature was decrease to 610°C after annealing. The group-III source used was trimethylindium (TMIn; $(CH_3)_3In$, 0.13 Pa) and the group-V sources used were tertiarybutylarsine (TBAs; $(CH_3)_3CAsH_2$, 5.4 Pa) and tertiarybutylphosphine (TBP, $(CH_3)_3CPH_2$, 9.0 Pa) The group-V gases were supplied over 200°C during heating up and shut off below 400°C during cooling. We measured X-ray photoelectron spectroscopy (XPS) and analyzed elements existing on the Si surfaces which had been annealed in three kinds of ambient: only H_2, TBAs and TBP.

3. Results and discussion

Surface state of Si after annealing

Figure 1 shows the atomic ratios of deposited elements on Si surfaces annealed in H_2, TBAs and TBP ambient, respectively. The values on the surface just transferred into N_2-purged glovebox attached to the MOVPE apparatus are also shown for reference. In addition to Si, C and O peaks, P peak was observed on the non-annealed surface due to contamination inside the glovebox. For the H_2- and TBAs- annealed surfaces, P can be contaminated also during annealing.

In the case of the H_2-annealed surface, trace amount of As, Ga and In were also observed due to the reactor contamination because these elements are frequently used in our reactor. A large amount of C was also observed, probably due to adsorbed reaction by-products on the surface of a reactor. This carbon contamination of the Si surface was reduced to the background level for the TBP- and TBAs-annealed surfaces, suggesting surface passivation of Si with

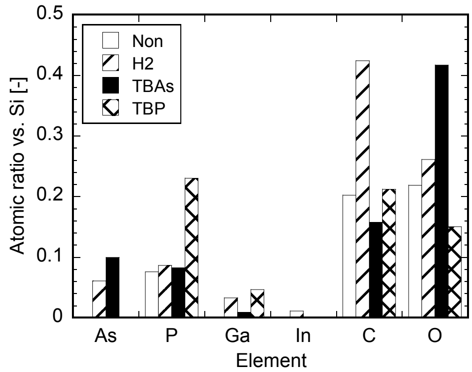

Fig. 1 Atomic ratios of six elements versus Si on Si surfaces annealed in H_2, TBAs and TBP ambient measured by X-ray photoelectron spectroscopy (XPS). The values on the surface just transferred into N_2-purged box are also shown for reference. X-ray source of XPS was Al Kα (1453.6 eV) and the take-off angle was 45°. These values were calculated from areas for each XPS peak corrected by the sensitivity factors.

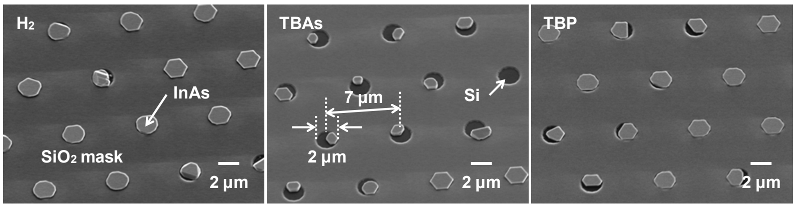

Fig. 2 Bird's-eye view SEM pictures for InAs islands on MC-SAG mask grown at 610°C for 5 minutes after annealing at 850°C in H_2, TBAs and TBP ambient, respectively.

group-V atoms is effective to prevent the surface contamination.

In the case of the TBAs-annealed surface, however, fraction of O was significantly larger than other surfaces. This is in contrast to the TBP-annealed surface, for which only a small amount of O atoms was observed. It is possible that TBAs-annealed Si surface is imperfectly covered with As. Uncovered fraction Si of surface was easily oxidized. Affinity between As and O probably promoted surface oxidation. This finding suggests that As is not suitable for surface passivation of Si, even when we want to grow III-arsenide layer on Si surface.

On the other hand, the TBP-treated surface was not oxidized significantly. This is probably because P atoms passivated Si surface completely at high temperature. In this sense, not As but P is suitable for surface passivation of Si prior to the growth of a III-arsenide layer. However, excessive high temperature promotes bond formation between surface P and Ga atoms which desorbed from inside of the reactor.

InAs growth after annealing

Figures 2 and 3 are the bird's-eye view scanning electron microscopy (SEM) pictures and 2θ-ω peaks of X-ray diffraction (XRD) from the (111) plane for InAs islands grown for 5 minutes after annealing in H_2, TBAs and TBP ambient as stated above.

Most of InAs islands on the H_2-annealed Si surface were grown laterally and buried Si growth areas, the shape of which were uniform. However, the number of islands which were grown incoherently was higher than those on substrates annealed in other ambient and plural nuclei were observed in some growth areas. XRD peak for InAs shown in Fig. 3 is also significantly broad, indicating the poor crystallinity. This poor crystallinity can be due to rough surface of these islands. Another possibility is that small plural nuclei were generated using a lot of contamination as a core and they were coalesced to a good-looking hexagonal island, i.e., a multi-domain island.

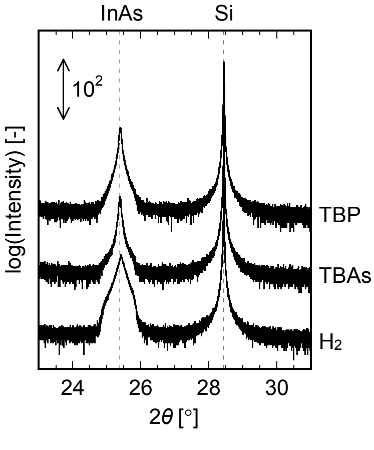

Fig. 3 X-ray 2θ-ω diffraction from the (111) plane for InAs islands corresponding to those shown in Fig. 2. Diffraction positions of relaxed single crystals are shown for reference.

On the other hand, the uniformity of the shape of InAs islands on TBAs-annealed Si was poor and Si surface was not buried by InAs although the XRD peak was sharp. In addition, nuclei did not emerge in some growth area. This non-uniformity of the shape or poor nucleation reflects the imperfect coverage of As atoms and the partial oxidization on Si surfaces.

In contrast, InAs islands on TBP-annealed Si were nucleated perfectly and most of them were grown laterally; the height of islands was smallest. Sharp XRD peak in Fig. 3 indicates the high coherency of islands. However, the shape of islands was random, that is, islands did not show the perfect hexagonal shape. This random shape is presumed to be because Ga contamination has an effect on nucleation of InAs or the substitution of P atoms with As atoms at the topmost of Si at the beginning of the growth was not successful.

4. Summary

We investigated the state of Si(111) surface and the effect on InAs growth after annealing at high temperature with and without TBAs or TBP in H_2 ambient in the MOVPE reactor. TBP-annealed surface is better in terms of the protection effect of surface contamination, the perfect nucleation and the lateral growth of InAs. However, Ga starts to re-desorb from inside of the reactor and adsorb on P-terminated Si surface at too high temperature, which may affect InAs growth. Accordingly, we should decide the proper annealing temperature to avoid adsorbing contamination on Si surface. Furthermore, we should also investigate how to switch from the flow of TBP to InAs growth, which TBAs is used.

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