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Abstract

We have studied effects of hydrogen treatment on the resistivity profile of the SiGe/Si episystem by spreading resistance (SR) method. In this paper, we present experimental findings that hydrogen treatment reduces the resistivity at a specific part in the Si substrate region. This position was confirmed to be under the interface between SiGe and Si that emerged on the bevel surface during hydrogen treatment. We investigated the depth of resistivity-reduced regions which was formed by various hydrogenating conditions and found that the region was extended to the same depth as the penetration depth of hydrogen. We concluded that the low-resistivity region was formed under the influence of hydrogen introduced from bevel surface. We attributed this resistivity reduction to formation of some defects which originally existed at the interface and diffused into Si substrate with hydrogen.

Keywords: SiGe/Si; hydrogen; resistivity reduction; interface
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1. Introduction

Hydrogen is one of the most common elements in semiconductor process, and hydrogen atoms are easily introduced into semiconductors to play various roles in semiconductors. One of the widely known effects of hydrogen is electrical passivation of acceptors in Si. It is also reported that hydrogen combines to electrically inactive carbon in Si to activate it to the contrary [1, 2]. On the other hand, SiGe film is a promising material as fast operating device materials or pseudosubstrate for strained Si devices. Usually, episystems have one or more heterointerface, and epifilms are often strained due to lattice misfit. Investigating influences of such condition on behavior of hydrogen is an important subject. For example, hydrogen is used in silicon-on-insulator process, and it is proposed that heterostructure of SiGe can be applied to surface layer exfoliation, which is a technique using the characteristic behavior of hydrogen in the strained lattice [3-5]. Recently, we reported that hydrogen reduced the resistance of *p*-type SiGe films [6]. We proposed the mechanism that hydrogen assists electrically-inactive boron atoms to combine with vacancies preferentially introduced in compressively strained SiGe, and they work as the shallow acceptor. In this research process, we found hydrogen treatment reduced the resistivity of a specific part in Si substrate, which means the formation of some defects that affected the resistivity. In this paper, we report experimental results about the formation condition of such defects and discuss the origin and relation to the interface.

2. Experimental

We prepare SiGe/Si episystem samples by molecular beam epitaxy (MBE) method. Si substrates we used were boron doped *p*-type Si wafers with resistivity of approximately 10 Ωcm. After chemically cleaning, the substrates were annealed at 750 °C for 2 h in the MBE chamber to remove the surface oxide, which is the process based on the Shiraki-Ishizaka method [7]. Then Si buffer layer with a thickness of 100 nm was deposited at 750 °C and subsequently SiGe single layer was grown at 500 °C without intentional doping. Si was evaporated by electron bombardment heating and Ge was evaporated from K-cell. We determined the film thickness by cross-sectional transmission electron microscopy. Germanium composition of the epifilm was calculated from the (400) peak angle of X-ray diffraction curve, based on the linear elastic theory. Here, we assumed the coherent growth of SiGe epilayer on Si substrate, which was confirmed by the fact that no cross-hatch pattern was observed by Nomarski optical microscope.

Spreading resistance (SR) method was used to measure the depth profile of resistivity. It must be noted that resistivity values of SiGe epilayer are not correct because we used calibration data of Si materials. However, this paper concerns the resistivity profile of Si substrate and we do not discuss that of SiGe layer. For the SR measurements, the sample was mechanically ground in a shallow angle θ (typically 0.5°) and bevel surface was probed.

Hydrogen treatment was performed using remote plasma at 110, 130, and 150 °C. Samples were set in a evacuated quartz tube with a diameter of 10 mm. Hydrogen gas of 40 sccm flowed in this tube and hydrogen plasma was operated in a microwave cavity

with an injection power of 50 W. Samples were laid parallel to the gas flow approximately 20 cm apart downstream from the cavity. In order to supply more hydrogen atoms to the sample [8, 9], water vapor of 2.0 sccm was mixed in the hydrogen gas. This treatment was performed after beveling the samples for the SR measurement in their as-grown state. Therefore, it is significant condition that the inner part of the SiGe/Si sample was exposed to the atmosphere during the hydrogen treatment.

3. Results and discussion

Typical depth profile of resistivity is shown in the upper part of Fig. 1. In as-grow state (open circles), resistivity at the interface between SiGe and Si is low. This resistivity reduction was already reported in our previous papers and explained by the concentration of excess boron acceptor [6, 10], which is probably identical to the phenomena reported as a boron spike in Si MBE [11, 12]. Here, we must refer the fact that a lot of electrically-inactive boron atoms also exist at the interface as well as electrically active ones, which was turned out by comparing both results of secondary ion mass spectroscopy and SR measurement [6].

In the profile after the hydrogen treatment at 130 °C for 2 h (filled square), another resistivity-reduced region was observed at the depth of approximately 3.5 μm. Before this measurement, bevel surface of the sample was reground and removed by a few microns. Taking account of the error in regrinding the bevel surface in parallel, the difference of depth between the two resistivity drops (approximately 3.0 μm) is

identical to the removed surface thickness d (d = 3.3 μm). We confirmed that when we repeated regrinding the bevel surface, the position of the second resistivity drop shifted into the deeper position corresponding to the removed thickness. The meaning of this position of the second resistivity drop can be easily understood by comparing the SR results and cross section of the sample that was illustrated in the lower part of Fig. 1. The darkly shaded part in Fig. 1 shows the region whose resistivity was reduced. It is obvious that the position of the second drop of resistivity is around the intersection of SiGe/Si interface and the hydrogen-treated bevel surface. At the time of measurements after hydrogen treatment, the initial bevel surface (dashed line) was removed and resistivity-reduced region was situated in the Si substrate apart from the SiGe epifilm. Therefore, the resistivity reduction has no relation to the band structure of the heterojunction. We presume that some kinds of defects which affected the resistivity were formed there.

Another characteristic of the resistivity profile after hydrogen treatment is the elevation of resistivity in the right side of the second resistivity drop. This is easily explained by passivation of boron acceptor in Si substrate by hydrogen. This characteristic can be used for confirmation of hydrogen incorporation into *p*-type Si. More interesting phenomenon is that no resistivity-elevation is observed in the left side of the second resistivity drop. This indicates that SiGe epifilm prevent hydrogen from penetrating into Si substrate, which was already reported and discussed elsewhere [10].

We investigated how deep the resistivity-reduced region was extended into the Si substrate from the hydrogen-treated surface. Figure 2 shows the resistivity profiles

measured after step-by-step regrinding the bevel surface for the hydrogen treated (150 °C, 20 min) sample. To avoid the complication, the each line of resistivity profile is drawn lower by one figure than the result of the preceding measurement. The resistivity drop can be seen still after removing bevel surface by 8.2 μm, and cannot be seen in the case of 10.7 μm. In brief, the defects were formed in the region which extent to the depth about 8.2 - 10.7 μm for this hydrogenating condition. We also notice that the resistivity elevation in the right side of the second resistivity drop disappeared simultaneously. This indicates that the penetration depth of hydrogen into Si substrate and the formation depth of defects were the same. To confirm this, we performed the same experiments for various samples that were hydrogen-treated under various temperature and time conditions. The results are shown in Fig. 3. In this figure, formation depth of each condition is shown as an error bar, whose top mark means the removed thickness of bevel surface at which the resistivity drop disappeared, and whose bottom mark is the removed thickness of just before that step. The horizontal axis is square root of the hydrogenation time *t*. Although data are considerably scattered, we can fit the data linearly for each temperature. When we assume the penetration depth is given by $2*(D_H t)^{1/2}$, we can calculate the diffusion coefficient of hydrogen $D_H = (m/2)^2$, where m is the slope of the fitted lines. The obtained D_H (cm^2/s) are $2.1*10^{-11}$ for 110 °C, $2.4*10^{-11}$ for 130 °C, and $1.5*10^{-10}$ for 150 °C. Taking account of the large experimental error, these are moderate value compared to the previous reported diffusion coefficient of hydrogen [13]. These results clearly show that the defect formation is attributed to the hydrogen atoms introduced from the bevel surface.

Our next interest is the origin of the defects. We must note again the location where the defects are formed. The defect-formed region is just under the interface between SiGe and Si which emerge on the bevel surface during the hydrogen treatment. The SiGe epifilm was grown coherently with the Si substrate and was compressively strained. Therefore, the interface is a singular face where the sign of stress field changes. To examine whether this characteristic of the interface is essential or not, we test a Si/Si sample, whose film growth condition is identical to the SiGe/Si. As shown in Fig. 4, however, the resistivity reduction was also observed in this case. Interface of our sample has another characteristic. As mentioned before, a lot of electrically inactive boron atoms exist around the interface. In our previous paper [6], we attributed the resistance reduction of SiGe film which contained electrically inactive boron atoms to the activation of such boron atoms under the influence of hydrogen. The present resistivity reduction may be the same mechanism. However, the results shown in Fig. 5 exclude this explanation. The solid line in Fig. 5 shows the resistivity profile of the sample that was hydrogen-treated at 130 °C for 120 min and subsequently annealed at 200 °C for 70 min. We cannot see the second resistivity drop in Si substrate. If the defects formed during the hydrogen treatment had persisted in existing after the annealing, the resistivity drop were observed at the depth position around 3.4 μm. In short, the formed defects were annihilated by the annealing at 200 °C. If substitutional borons were formed and worked as acceptors, such thermal instability cannot be explained. However, the possibility is not excluded that electrically inactive boron atoms at the interface have some relation to the defects. The origin of the defects is not so clear at present, but we

suspect it as below. A part of excess boron atoms at the interface may be initially in cluster-like state and electrically inactive. They interacted with hydrogen atoms to diffuse into Si substrate and to form some charge-up defects with gap state, and hole-accumulated region was formed in *p*-Si substrate.

4. Conclusion

We found that hydrogen treatment using remote plasma causes a resistivity reduction at specific site in Si substrate that is under the interface between SiGe and Si that was emerged on the bevel surface during hydrogen treatment. We investigated the formation depth of this resistivity-reduced region and found that it was coincident with the penetration depth of hydrogen. Therefore, we concluded that the hydrogen atoms which were incorporated from the bevel surface caused the resistivity reduction. Since excess boron atoms exist at the interface of our sample, we supposed that some boron-related defects might have relation to the reduction of the resistivity. However, the defects are thermally instable and annihilate at 200 °C, which means that they are not originated from isolated substitutional boron atoms which are common acceptor.

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Fig. 1. Typical depth profile of resistivity before and after hydrogen treatment using remote plasma (upper part) and the cross section of the sample (lower part). The lateral position of the lower illustration corresponds to the horizontal scale of the upper graph. Dashed lines shows the surface and interface during hydrogen treatment, and solid lines shows the surface where the resistivity profile after the treatment was measured.

Fig. 2. Resistivity profiles measured after step-by-step regrinding the bevel surface. Total removed thickness of bevel surface is shown as *d*. For avoiding the complication, each profile is shifted downward by one figure compared with the preceding result. Short arrows indicate the position of the second resistivity drop or the position expected to be observed.

Fig. 3. The limit of the depth that the defects were formed (formation depth) under various hydrogenating conditions. Circles, squares, and triangles show the results of 150 °C, 130 °C, and 110 °C, respectively. The lines crossing at the origin are the results of linear approximation of the data for each temperature.

Fig. 4. Depth profiles of resistivity of Si/Si sample before and after hydrogen treatment at 130 °C for 120 min. The bevel surface was removed by the thickness of 1.9 μm before the SR measurement for the hydrogen-treated sample.

Fig. 5. Depth profiles of resistivity of SiGe/Si before and after hydrogen treatment at 130 °C for 120 min and subsequent annealing at 200 °C for 70 min. The bevel surface was removed by the thickness of 3 μm after the treatments.