Annealing behavior of hydrogen-plasma-induced *n*-type HgCdTe

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In this letter, the effect of annealing in plasma-induced-type converted HgCdTe was observed. The Hg deficient annealing process reconverts the type converted n-HgCdTe into p-type. The activation energy of the process was determined to be 0.99eV regardless to the gas species used for the type conversion process. However, the absorption edge moved toward short-wave direction for hydrogen-plasma-treated sample. The absorption edge shift was observed even after the annealing process, which means the passivation and junction formation are separate phenomena. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2043239]

The *p*-to-*n* type conversion processes using plasma in $Hg_{1-x}Cd_xTe$ alloy are recently developed and are still under investigation.[1] The plasma induced type conversion process provides n^+-n^--p junction structure without the additional annealing process as in ion implant process.[2] Various types of the plasma sources, such as reactive ion etch[3] (RIE) or inductively coupled plasma[4] (ICP), can be used for the type conversion process. All of the processes can form a deep junction in a short time. Many kinds of gas mixture can be used for the process as well. In this research, we have adopted hydrogen-containing plasma incuded process for the type conversion of HgCdTe surface because it is known that the process yields hydrogen passivation effect and small damage of hydrogen atom.[5]

The stability of hydrogenated semiconductor device has been interested. The stability of the HgCdTe device is also a point of interest. It is mainly because that the electrical properties of HgCdTe can be changed during the baking process above 150 °C.[6] Smith *et al.*, moreover, reported that the RIE induced junctions are completely removed after 200 °C for 17 h of annealing.[7]

The junction formation mechanism is still an open question for the hydrogen plasma induced junction formation process. There are two possibilities of the mechanism of type conversion in hydrogen plasma induced *p*-to-*n* type conversion process. First possible mechanism is related with Hg interstitial, which is known to be created during the plasma process and diffuses into the HgCdTe.[8] In this mechanism, the Hg interstitials themselves act as donor, or excess Hg interstitials recombine with Hg vacancies to reveal a grown-in background donor. This mechanism can widely be applied to ion implantation, ion beam milling, and plasma process. The other mechanism is proposed as hypothesis, which can especially be applied to hydrogen-containing plasma type conversion process.[9] In the mechanism, the hydrogen atoms act as donor just like in other semiconductors[10] or the hydrogen atoms passivate vacancy-related acceptors of HgCdTe crystal to reveal background donor. The hypothesis is based on the assumption that only very small damage would be applied to the HgCdTe crystal during the hydrogen plasma induced junction formation process, and relatively few Hg interstitial would be generated during the process. Thus, the hydrogen atoms would directly participate during the junction formation process as described above.

The baking stability of the plasma-induced junction and the hydrogen in HgCdTe, in this paper, was simultaneously investigated with Hall measurement and infrared transmission spectra. From the annealing behavior of junctions, the type conversion mechanism for the plasma-induced junction formation process was also investigated.

Hg vacancy doped $Hg_{0.77}Cd_{0.23}Te$ wafers were used which were grown by solid state recrystallization (SSR) method with a hole concentration of $5\sim10\times10^{15}/cm^3$ and mobility of $400-600\ cm^2/V\ s$. The type conversion processes were performed by inductively coupled plasma chamber without any passivation layer on HgCdTe, and H_2 or Ar gas was used for the type conversion process. The process time and plasma rf power were fixed to 5 min and 200 W, respectively. After the type conversion process, 1 μm of the HgCdTe layer was chemically etched to remove damaged HgCdTe. The wafers were baked in convection oven at 150, 190, and 210 °C. This process would be a mercury-deficient annealing condition. The Hall measurement is performed at 77 K using Van der Pauw method, and the infrared transmission spectra are measured at room temperature.

Figure 1 shows the temperature-dependent Hall coefficient and mobility of the type converted HgCdTe wafer using

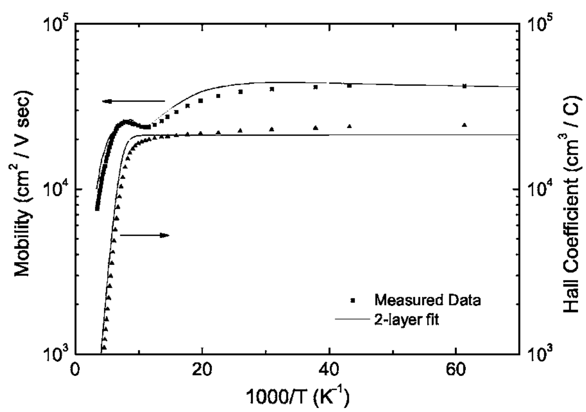

FIG. 1. Temperature dependent mobility and Hall coefficient of the type converted HgCdTe wafer; anomalous Hall effect was fitted into the layer model.

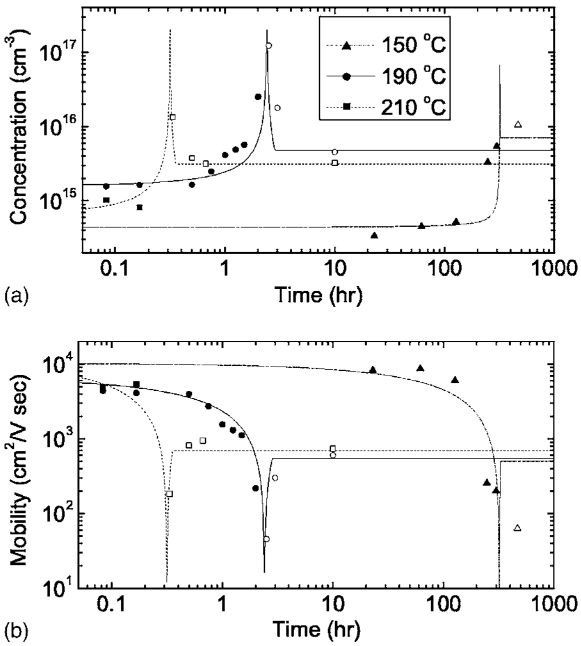

FIG. 2. Carrier concentration and mobility change according to baking process; filled and open data points are *n*-type and *p*-type, respectively. (a) carrier concentration change of hydrogenated wafer; (b) carrier mobility change of hydrogenated wafer.

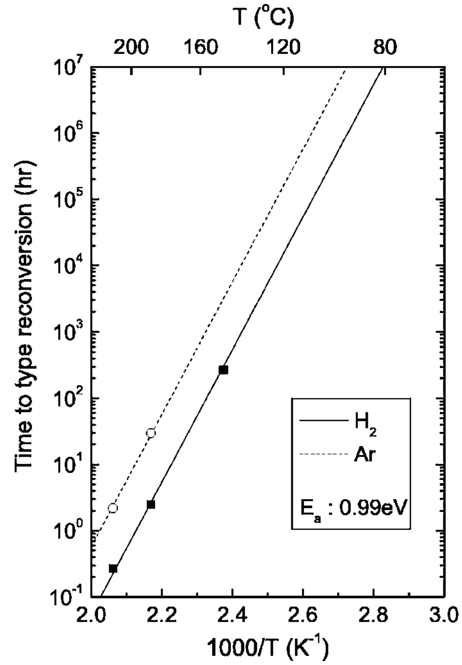

FIG. 3. Time taken for type reconversion according to the annealing time; activation energy of the process has no relation to the species of gas used during type conversion process. The difference between the two processes is due to the initial junction depth difference.

hydrogen plasma. The data shown in Fig. 1 has anomalous peak around 150 K. The anomalous peaks in HgCdTe can be modeled into layer model[11] or inhomogeneity model.[12] The two kinds of model involve the assumption that both *n*-type and *p*-type regions exist simultaneously in HgCdTe crystal. In our case, we expected the p-to-n type converted region at the top of the wafer, and a large portion of the bulk wafer remained as p-type. Thus, the layer model would be more preferred for this case. In the layer model, the Hall coefficient and the conductivity of the wafer are expressed as

$$R = \frac{d\sum_k q_k \int_0^d n_k(z)\mu_k^2(z)dz}{(q\sum_k \int_0^d n_k(z)\mu_k(z)dz)^2} \quad (1)$$

$$\sigma = \frac{q}{d}\sum_k \int_0^d n_k(z)\mu_k(z)dz, \quad (2)$$

where total thickness is d, n_k and μ_k is k^{th} layer concentration and mobility. Total carrier mobility and concentration of the wafer can be easily obtained from the equation (1) and (2). The fitting curves are determined by the Cd composition, empirical fomulas of the band gap, intrinsic carrier concentration,[13] hole mobility, and electron mobility.[11] The fitted results for the mobility and Hall coefficient are displayed in Fig. 1. Thus, it can be describe that the layer model can successfully describe the Hall data of the wafer which contains plasma-induced junction.

Figure 2 shows the carrier concentration and mobility change according to the annealing time and temperature. Filled data points are *n*-type conductivity, whereas open data points are *p*-type conductivity. All wafers show the n-type conductivity just after type converted, and their junction depths are about 50 μm from the top of the HgCdTe surface. The carrier concentration and mobility data show sharp peaks just before and after the type reconversion. The type converted *n*-layer is disappeared after long-time annealing process. In order to analysis this phenomena, the layer model for Hall data interpretation was adopted with simple additional parameter. Each sample is modeled into the original p-type bulk layer and the type converted n-layer. From the previously proposed junction formation mechanism, the species of diffusion during the annealing process is assumed to be Hg interstitial, Hg vacancy, and hydrogen atom. As a result of simulation of the diffusion process, the n-layer thickness change can be approximately proportional to square root of the process time. So, the thickness of the type converted n-HgCdTe layer can be written as simple following equation:

$$d_{\mathrm{n}} = d_{\mathrm{n,initial}} - \sqrt{C_0 \cdot t \cdot \exp(-E_a/kT)}, \quad (3)$$

where d, t, and E_a is thickness, annealing time, and activation energy, respectively. The constant C_0 includes Arrhenius parameter and doping concentration of the species. For the modeling of the doping concentration and mobility change according to annealing time, Eqs. (1)–(3) should be considered together. In Fig. 2, the calculated results are shown for the various annealing temperature of hydrogen plasma induced junctions. Both the carrier concentration peak and mobility peak can be well matched with the model.

In order to get the annealing time required for the type converted n-region being almost disappear, the Eq. (3) can be modified following form:

$$t_{\mathrm{recover}} = C_1 \cdot \exp(E_a/kT). \quad (4)$$

The constant C_1 includes C_0 and initial junction depth. Figure 3 shows the recovery time modeled from Eq. (4) according to the annealing temperature. In the Fig. 3, the activation energy of the diffusion process is clearly observed. Both of the hydrogen plasma induced junction and the argon plasma induced junction showed the activation energy of 0.99eV.

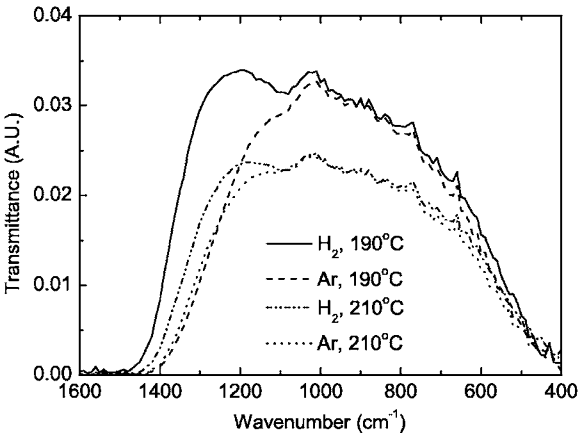

FIG. 4. Infrared transmission spectra of 10 h annealed HgCdTe wafers; even though the wafers are completely reconverted into *p*-type, the passivation effect of hydrogen can be observed.

There have been some reports about annealing behavior of HgCdTe under Hg ambient. It is known that the carrier concentration and junction depth of the HgCdTe are determined by the annealing temperature and Hg partial pressure, and the annealing process time. The activation energy of Hg diffusion is known as 1.01eV for junction formation process.[14] From these results, the *n*-to-*p* type reconversion process would be mainly affected by mercury diffusion process, regardless of the gas species used during the type conversion process. The difference between the two lines is originated from the initial junction depth, which is determined by process conditions. It is expected, and shown in Fig. 3 that the argon plasma induced junction depth is deeper, because the argon plasma gives more damage than the hydrogen plasma.

It has been reported that the defect concentration of the HgCdTe can modify the absorption edge and the hydrogen passivation enhances infrared transmissions near absorption edge.[15] In order to investigate hydrogen passivation effect of hydrogen plasma induced junction formation process, infrared transmission spectra measurement was performed. Figure 4 shows the infrared transmittance of HgCdTe samples at 300K. The sample was plasma induced *p*-to-*n* type converted, sufficiently annealed, and reconverted so that its conductivity type is to be *p*-type. The hydrogen plasma treated HgCdTe shows the sharp absorption edge and absorption edge shift compared to the argon plasma treated HgCdTe. From this result, we can point out two facts: First, HgCdTe type conversion phenomena were observed for every plasma process regardless of the gas species used for the process. But the hydrogen plasma induced type conversion process has an advantage because of its hydrogen passivation effect. Second, the hydrogen passivation effect can be retained after thermal annealing process, even after the plasma-induced junction vanished.

From the results of the annealing and infrared transmission, the junction formation mechanism can be clarified. It is clear that the argon plasma induced junction formation process follows Hg interstitial related mechanism, because the argon atom itself cannot act as donor or combine with other atoms in HgCdTe crystal. The activation energy of the argon plasma and hydrogen plasma induced junctions are exactly same, which is similar with already reported Hg interstitial diffusion value. Hence, it is supposed that the type conversion mechanism of hydrogen plasma induced junction formation would be same with the argon plasma case.

We have investigated the effect of annealing in plasma induced type converted HgCdTe. The Hg deficient annealing process reconverts the *n*-type HgCdTe into *p*-type, and the activation energy of the process have no relation with the gas species used for junction formation. The absorption edge is moved toward short wave direction for hydrogen plasma treated sample. So, the hydrogen plasma induced junction formation process is beneficial because the process provides type conversion and passivation effect simultaneously. The absorption edge shift is observed even after the junction vanished, which means the passivation and junction formation are separate phenomena.

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