Arsenic flux dependence of incorporation of excess arsenic in molecular beam epitaxy of GaAs at low temperature

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(Received 12 May 1998; accepted for publication 14 July 1998)

Incorporation of excess As in GaAs layers grown by molecular beam epitaxy was studied by varying As fluxes for four different substrate temperatures, 210, 240, 270, and 290 °C. Concentrations of excess As in GaAs layers were estimated by measuring increases of lattice spacings with x-ray diffraction, and the substrate surface temperature was monitored by using a quartz rod connected to an infrared pyrometer with its end placed in the vicinity of the substrate surface. Nearly stoichiometric GaAs layers without any detectable increase of the lattice spacing are grown at all substrate temperatures under the As atom flux equal to the Ga atom flux. With a slight increase of the As flux from the above stoichiometric condition, the concentration of excess As sharply increases for all substrate temperatures. For the substrate temperature of 210 °C, the concentration of excess As is saturated in the range of As atom fluxes more than three times the Ga atom flux, while similar tendencies are observed for other substrate temperatures. The incorporation process of excess As is discussed on the basis of these results. © *1998 American Institute of Physics.* [S0003-6951(98)00437-9]

GaAs layers are normally grown by molecular beam epitaxy (MBE) at substrate temperatures near 600 °C with As_4/Ga flux ratios more than a few tens in beam equivalent pressures (BEP) at growth rates around 1 μm/h.[1] Under this condition, stoichiometric GaAs layers having high crystalline qualities are obtained with their composition being nearly independent on the growth parameters. When the substrate temperature is lowered to the range between 200 and 300 °C with other parameters kept at the normal condition, highly nonstoichiometric GaAs layers with excess As around 1% but still possessing high crystalline quality are obtained.[2,3] The concentration of excess As in a GaAs layer grown at the low substrate temperature by MBE (LT-GaAs) is extremely large in comparison with those in the equilibrium phase diagram where the concentration of excess As is only 0.1% at most near the melting point.[4] Due to novel electrical and optical properties of as-grown and annealed LT-GaAs which result from high concentrations of excess As, a large number of researches have been carried out on this material, aimed at its device applications.[5,6] Up to the present, however, there has been almost no study which tries to elucidate the incorporation process of excess As in the low temperature growth of GaAs by MBE.

According to recent studies, the concentration of excess As in LT-GaAs is known to change with the growth condition. The substrate temperature appears to affect the concentration most significantly. The excess As sharply increases as the substrate temperature is lowered.[7–9] In a conventional MBE system, the substrate temperature is controlled by using a thermocouple placed at the backside of the substrate holder. The temperature indicated by the thermocouple, hence, differs more or less from the substrate surface temperature. In addition, the difference between the substrate surface temperature and the temperature indicated by the thermocouple is significantly affected by a slight variation of the location of the substrate holder with respect to that of the thermocouple. It is, therefore, extremely difficult to control the substrate surface temperature reproducibly from one growth experiment to another. For this reason, the quantitative relationship of the concentration of excess As in LT-GaAs to the growth temperature has not been fully understood to date. The concentration of excess As in LT-GaAs is also known to be affected by the flux condition. It was reported that high quality GaAs layers with very few point defects due to excess As could be grown even at substrate temperatures close to 200 °C if As fluxes were kept comparable to Ga fluxes.[10] Reflection high energy electron diffraction (RHEED) intensity oscillations were also observed at low growth temperatures in a certain range of the ratio of As and Ga fluxes.[11,12] In this letter, we present the results of measurements of concentrations of excess As in LT-GaAs layers as a function of As_4 fluxes for four different substrate surface temperatures which were carefully controlled in order to achieve good reproducibility. The incorporation process is discussed on the basis of the results.

GaAs layers were grown in a MBE chamber which had effusion cells for Ga, As_4, In, Si, and Be, equipped with a RHEED system. GaAs substrates with the (001) orientation were mounted on a Mo holder with indium. In order to achieve good reproducibility of the substrate surface temperature, the same holder was used, and the size of substrates was kept constant for all growth experiments. The substrate was rotated at a rate of 7 rpm during the growth which resulted in the uniformity of fluxes as well as thermal radiation from the Ga cell over the growth surface. After the oxide desorption and the annealing for 10 min at 600 °C, an undoped GaAs buffer layer with a thickness of 160 nm was grown at 580 °C at a growth rate of 0.9 μm/h, and the sub-

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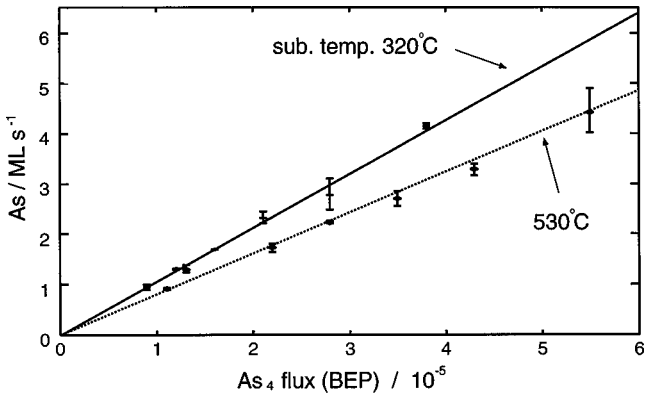

FIG. 1. Relationship of As atom fluxes which are incorporated into grown layers with As_4 fluxes in BEP. Data on the solid line and dotted line were obtained by the measurements of RHEED intensity oscillations at 320 and 530 °C, respectively.

strate temperature was lowered to that for the growth of a LT-GaAs layer.

All LT-GaAs layers were grown at the growth rate of 0.9 μm/h for 40 min to a thickness of approximately 640 nm. Four different substrate temperatures, 210, 240, 270 and 290 °C were employed for the low temperature growth. Prior to each growth of a LT-GaAs layer, the substrate surface temperature was measured by using an infrared pyrometer. In order to avoid radiations to the pyrometer from other parts of the growth chamber, the surface temperature was measured through a quartz rod with 590 mm in length and 6 mm in diameter which was covered by a stainless steel tube. One end of the quartz rod was faced to the sensor head of the pyrometer which was placed in the outside of the growth chamber, and the other end of the quartz rod was brought close to the substrate surface at a distance of approximately 3 mm for the measurement. The calibration of the pyrometer with the quartz rod was made by using melting points of Sn and Pb. The growth of a LT-GaAs layer was initiated after the substrate temperature was sufficiently stabilized. The substrate temperature was measured again in the same manner 1 min after the finish of the growth. The temperature measured after the growth was always several degrees higher than that measured before the growth, which is ascribed to the radiation from the Ga effusion cell during the growth as reported in a recent letter.[13] In this letter, substrate surface temperatures measured before the growth are referred as growth temperatures of LT-GaAs layers, the error of which was primarily caused by the position of the quartz rod end with respect to the substrate surface and found to be within 1 °C.

As_4 fluxes were measured with an ionization gauge placed at the position of the substrate. In this study As_4 fluxes were varied in the range between 0.87×10^{-5} and 8.0×10^{-5} Torr in BEP. For certain As_4 fluxes measured with the ionization gauge, As atom fluxes which were supplied to the growth surface were measured by using RHEED intensity oscillations[14] at 320 °C where exactly a half of As atoms in As_4 molecules arriving at the growth surface are incorporated into the growth layer, according to a recent study.[15] In Fig. 1, As atom fluxes arriving at the growth surface, which were measured with the RHEED intensity oscillations, are plotted as a function of As_4 fluxes in BEP

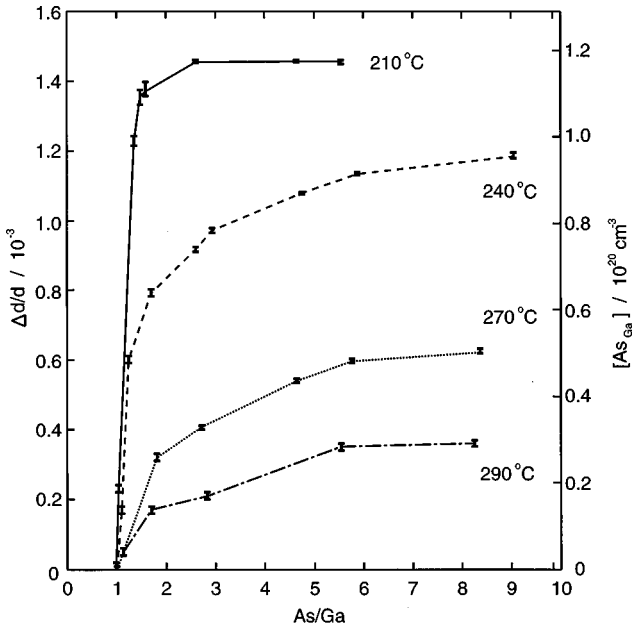

FIG. 2. Changes of lattice spacings of LT-GaAs layers as a function of the ratio of As and Ga atom fluxes. Concentrations of antisite As corresponding to changes of lattice spacings (see Ref. 19) are also shown in the figure.

for both 320 and 530 °C. In order to avoid a significant variation of the As_4 flux during the growth, the temperature of the As effusion cell was stabilized for more than 2 h prior to each growth experiment. The As_4 flux in BEP was measured again 3 min after the completion of the growth.

Changes of lattice spacings of LT-GaAs layers from that of the substrate GaAs were determined by rocking curve measurements of (004) reflections by using an x-ray diffractometer with a four crystal monochrometer. The Cu $K\alpha$ radiation was used for the measurement. In the case of small changes of lattice spacings where (004) peaks of LT-GaAs layers were not fully separated from those of substrates, the changes were estimated by comparing observed rocking curves with those calculated with the Takagi-Taupin equation of the dynamical diffraction theory.[16] For the calculation, it is assumed that all excess As atoms occupy antisite positions and lattice spacings vary linearly with concentrations of excess As, according to an earlier report.[17–19]

Figure 2 shows changes of lattice spacings of LT-GaAs layers, $\Delta d/d$, as a function of the ratio of the As atom flux to the Ga atom flux for four growth temperatures. Here, the As atom flux corresponds to that measured at 320 °C with RHEED intensity oscillations under the condition that the growth rate is limited by the As flux. The change of the lattice spacing, $\Delta d/d$, is known to vary linearly with the concentration of excess As which occupy antisites.[19] In this letter, therefore, we discuss the results by assuming that the concentration of excess As, which includes interstitial As atoms and Ga vacancies besides antisite As atoms, is represented by the change of the lattice spacing, $\Delta d/d$. In Fig. 2, one first notes that at all four growth temperature stoichiometric GaAs layers are obtained under the flux condition of the As atom flux equal to the Ga flux. Here, the stoichiometric layers mean that their lattice spacings are the same as that of the GaAs substrate within the detection limit of the x-ray diffraction technique. This result implies that even in

this temperature range GaAs layers are grown via the surface reaction of two adsorbed As_4 molecules which leaves only four As atoms in the growing layers out of eight As atoms involved in the reaction. Next it is noted that concentrations of excess As sharply increase with slight increases of the As atom flux from the stoichiometric condition. This result indicates that significant concentrations of excess As are incorporated into the growing layers once the As atom flux slightly deviates from the exact stoichiometric condition. Finally, one notes that the concentration of excess As becomes constant in the range of the As atom flux being three times greater than the Ga atom flux at the growth temperature 210 °C. At other growth temperatures, the concentration of excess As continues to increase in the whole flux ranges used in this study, but the tendency of the saturation is also observed at these temperatures. With the result shown here, it should be pointed out that the dependence of the incorporation of excess As on the growth temperature cannot necessarily be discussed in a meaningful way if it is examined under an arbitrarily chosen flux condition.

The dependence of the concentration of excess As on the flux condition, shown in Fig. 2, resembles the Langmuir adsorption isotherm where the sticking probability of molecules is proportional to the fraction of unoccupied surface sites.[20] With this similarity one can suggest the following model of the incorporation process of excess As. It is known that GaAs(001) surface reconstructions such as $(2\times4)\gamma$ and $c(4\times4)$ have excess As atoms as a form of chemisorbed As dimers on the normal surface As atoms.[21,22] It is, therefore, assumed that these chemisorbed As atoms serve as a precursor of excess As atoms in the LT-GaAs layer and the saturation of the concentration of excess As in the range of high As atom fluxes results from the complete occupation of all available surface sites by chemisorbed As atoms as in the case of the Langmuir adsorption. The concentration of excess As in the LT-GaAs layer is, however, only 1% or 2% at most, while the complete occupation of surface sites by chemisorbed As atoms corresponds to the 100% concentration of excess surface As atoms. This large difference can be ascribed to reevaporations or site changes of chemisorbed atoms as a result of a highly unstable state at the transition from the precursor state to the final form of an excess As atom in the LT layer. These reevaporations and site changes should be thermally driven, and, hence, their rates should increase with raising the temperature. As expected from this model, Fig. 2 indicates that the saturated concentration of excess As in the high As atom flux range increases with lowering temperature. The saturated concentration at 210 °C, however, appears to be somewhat smaller than expected from the concentrations at the other three higher temperatures, when one considers the Arrhenius-type relation. Other factors besides that described above, such as lattice strains, may affect the maximum concentration of excess As. Further experimental studies are needed in order to fully clarify the incorporation process of excess As.

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