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THE DISTRIBUTION OF Sb ATOMS IN δ-DOPED SILICON CRYSTAL*

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The distribution of Sb atoms in δ-doped silicon crystals grown by molecular beam epitaxy at different temperatures was measured using the technique of synchrotron radiation X-ray low angle reflection. The results indicate that the doped Sb atoms are distributed exponentially in the epitaxial layers, and the 1/e decay lengths are 0.45, 0.95 and 3.5 nm for the samples grown at temperatures of 250, 300 and 350 °C, respectively. For samples grown at 400 °C, the 1/e decay length of the Sb atomic distribution increases drastically because of the segregation of Sb atoms during the growth process.

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I. INTRODUCTION

Recently, with the development of low-dimensional material science and techniques, local intense impurity-doping in Si crystals has attracted the interest of many researchers. With its distinctive electronic and photoelectronic properties, this kind of material shows broad prospects in applications.[1,2] For example, δ-doped Si and GeSi could be used in high speed and high density memory devices; Sb δ-doped Si crystal shows promising potential in wave-length selectable infrared light detectors of high efficiency. The properties of δ-doped semiconductors depend strongly on their microstructures such as the distribution region and density of the dopants, since these determine the width and depth of the quantum well. Sb atom is the most favoured n-type dopant in Si molecular beam epitaxy (MBE). However, the δ-doping of Sb atoms in Si MBE layer is restricted by the strong surface segregation of Sb atoms during the MBE growth.

The surface segregation of impurity atoms in Si crystal during MBE growth has been investigated in detail since the late 1980s. Barnett and Greene[3] suggested a critical temperature T^* to distinguish the thermal equilibrium region and the kinetically limited region. For temperatures below T^*, i.e., the kinetically limited region, the surface segregation can be greatly reduced to grow the required samples. Jorke[4] proposed a semi-empirical model of two-state-exchange, which assumed that the exchange of atoms occurred only between

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the surface and subsurface states to explain the surface segregation phenomenon. A formula for the 1/e decay length (related to the growth temperature T and the growth rate R) was obtained, and used to analyse the surface segregation of Sb atoms in Si crystals grown at 400–700 ℃ with a dopant area density of 10^{13}–10^{14} atoms/cm^2.

Since the doped atoms in the δ-doped crystals are quite few in number and are restricted to a very narrow region as thin as several nanometers, it is very difficult to measure their distribution by conventional structural analysis methods. The technique of synchrotron radiation X-ray low angle reflection, due to its high brilliance and good depth resolution, has been employed to measure the distribution of δ-doped atoms in the surface layers. Slijikerman *et al.*[5] and Xiu *et al.*[6] have used this technique to investigate the distribution of δ-doped Sb atoms in Si crystals grown by solid phase MBE. Both exponential-shaped (with a 1/e decay length τ=1 nm) and Gaussian-shaped (with a standard deviation of σ=0.7 nm) distributions of Sb atoms have been observed.

In this paper, the Sb atomic distribution in δ-doped Si crystal grown by MBE at different temperatures were measured by synchrotron radiation X-ray low angle reflection in order to find the optimum growth temperature for δ-doping. Results show that the δ-doping of Sb atoms in MBE Si layers can be realized when the growth temperature is below 300 ℃, and the distribution profile of the dopants are exponential-shaped with a 1/e decay length of 0.9 nm (300 ℃) and 0.5 nm (250 ℃). Most of the Sb atoms segregated to the surface in the sample grown at 400 ℃ so that no Sb atoms are detected in the MBE layer by X-ray reflection.

Ⅱ. SURFACE SEGREGATION AND DISTRIBUTION MODEL OF THE IMPURITY ATOMS

The concept of δ-doping in semiconductors assumes that the impurity atoms occupy only one monolayer in the crytal, forming a δ-function-like distribution as seen along the crystal normal. However, during the epitaxial growth, the potential of Sb atoms at the subsurface sites in higher than that of Sb atoms at the surface sites. Thus there is a tendency for Sb atoms to move from subsurface sites to the surface sites. This phenomenon known as the surface segregation, which makes the Sb atoms spread over the whole layers and is strongly influenced by the growth temperature. At high temperature, the surface segregation will be very strong, and all the doped atoms will move to the surface during the MBE process. The greater the thermal excitation, the stronger the segregation of the impurity atoms. In practice, for samples, grown at proper temperatures, the doped atoms will be distributed homogeneously on the epitaxial lateral plane, with some profile broadening along the normal of the epitaxial layers because of the surface segregation effect. This means that the distribution of Sb atoms in the Si epitaxial layer is one-dimensional.

We will now discuss the distribution model for δ-doped Sb atoms in the Si epitaxial layer according to the surface segregation of Sb atoms. The discussion is based on the following assumptions (see section Ⅲ for the sample preparation procedures):

(i) Since the diffusion coefficient of Sb atoms in crystalline Si at temperatures below 400 ℃ is so small that the diffusion of Sb atoms can be ignored[7], in our δ-doped samples,

the distribution of Sb atoms decreases very fast in the substrate Si crystal. There is a very steep variation of the Sb atomic distribution on the substrate side.

(ii) The desorption loss of Sb atoms is negligible at growth temperatures below 400 °C.[8]

(iii) The segregation occurs by atom movement between the surface and subsurface states.[4] That is to say, only the segregation of impurity atoms from the subsurface state to the surface state will be included.

Based on the above considerations, the growth procedures of the δ-doped Si samples can be described as follows. After the deposition of an Sb monolayer (the zeroth layer) on the Si buffer layer, (refer to section Ⅲ for the sample structures) the Si cap is grown one layer after another by MBE. During the deposition of the first Si cap layer, the Sb atoms have a tendency to segregate to the surface (the first Si layer) because the energy of the surface state is lower for the Sb atoms. This tendency remains untill the second Si cap layer is finished. At this moment, the segregation of Sb atoms from the Sb monolayer to the first Si cap layer stops while the Sb atoms already in the first Si cap layer move further outwards to the surface (i.e., to the second Si cap layer). This movement will not stop until the third Si cap layer is finished. This segregation process continues during the growth untill all the cap layers (assuming a total of t layers) are desposited.

According to the discussion above and the layer notation illustrated in Fig.1, we can obtain a distribution model for the dopant atoms in the MBE layers. As the growth temperature T and the rate of deposition R are kept constant during the MBE growth process, whenever a new surface layer (jth layer) has been deposited, the ratio of Sb atoms remaining

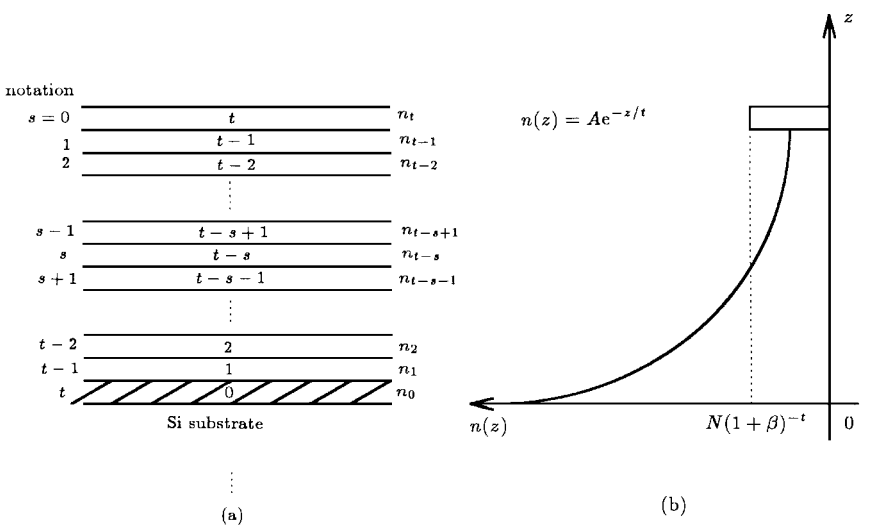

Fig.1. Sketch map of the epitaxial layers.

in the $(j-2)$th layer to the segregated Sb atoms (localised in the jth and $(j-1)$th layer) remains constant. This means that the following relationship is valid in the epitaxial layers:

$$\frac{n_{t-s}}{\sum_{j=t-s+1}^{t} n_j} \equiv \beta \qquad (s = 1, 2, \cdots, t) \ , \tag{1}$$

where n_j is the number of Sb atoms remaining in the jth layer, and $\sum_{j=t-s+1}^{t} n_j$ is the sum of Sb atoms over all the layers above the $(t-s)$th layer (see Fig.1(a)). The β is actually the reciprocal of the segregation coefficient, according to the definition. The larger β is, the smaller the effect of segregation.

From Eq.(1) it is easy to obtain the number of Sb atoms in the $(t-s)$th layer

$$n_{t-s} = \beta(1+\beta)^{s-1} n_t \qquad (s = 1, 2, \cdots, t) \ . \tag{2}$$

If the total number of doped atoms is N, then

$$N = \sum_{j=0}^{t} n_j = \sum_{s=0}^{t} n_{t-s} = n_t + \sum_{s=1}^{t} \beta(1+\beta)^{s-1} n_t \tag{3}$$

and we get

$$n_t = N(1+\beta)^{-t} \ . \tag{4}$$

By substitution of Eq.(4) into Eq.(2), we have

$$n_{t-s} = N\beta(1+\beta)^{-[(t-s)+1]} \qquad (s = 1, 2, \cdots, t) \ . \tag{5}$$

For the Si(400) plane, the atomic layer distance is $a_0/4$ and a_0 is the Si crystal lattice constant. The distance from the $(t-s)$th layer to the Sb monolayer is

$$z = (t-s) \cdot a_0/4 \ . \tag{6}$$

So the Sb atomic distribution in the Si epitaxial layers is then given as

$$n(z) = \frac{N\beta}{1+\beta}(1+\beta)^{-z/(a_0/4)} = \frac{N\beta}{1+\beta} \exp\left(\frac{-z\ln(1+\beta)}{a_0/4}\right) \qquad 0 \le z < t \cdot a_0/4 \ . \tag{7}$$

That is, the distribution of Sb atoms in the Si layers is Gaussian (in practice, it is a step distribution). We can approximate it as a continuous analytic function $n(z) = A\mathrm{e}^{-z/\tau}$, where A is a constant and

$$\tau = \frac{a_0}{4\ln(1+\beta)} \tag{8}$$

is the 1/e decay length of the distribution.

Since the diffusion of Sb atoms into the Si crystal is negligible, the distribution of Sb atoms under the Sb monolayer can be taken as zero, forming a steep gradient in the Sb-Si interface. Thus, the distribution of Sb atoms in the whole sample is

$$n(z) = \begin{cases} A\mathrm{e}^{-z/\tau} & 0 \le z < \frac{a_0 t}{4} \ , \\ N(1+\beta)^{-t} & z = \frac{a_0 t}{4} \ , \text{ at the surface} \ , \\ 0 & z < 0, \text{ in the Si substrate} \ . \end{cases} \tag{9}$$

It is obvious from Eq.(9) that when the segregation is serious, i.e., when $\beta \ll 1$, a large quantity of Sb atoms ($\sim N(1-\beta)t$) will move to the surface step by step in the growth

process, and only a few Sb atoms ($\sim N\beta t$) are exponentially distributed in the epitaxial layers. Actually, since the 1/e decay length is very long ($\tau \sim a_0/4\beta$), the distribution can be treated as being homogeneous. This conclusion is the same as that found in the literature.[3,4] Only in the case of weak segregation (large β) do very few Sb atoms segregate to the surface, while most of the dopant atoms are left in the epitaxial layers in an exponential distribution.

Ⅲ. EXPERIMENT

The samples used in the experiments were grown by MBE (Riber EVA-32 system)[9] at the State Key Laboratory of Surface Physics in Fudan University. The Si(400) substrate was cleaned by the Shriaki process[10], and then it was heated to 300 ℃ for 10–20 min in the preparation chamber under a vacuum of 1.33×10^{-6} Pa. The oxidation layer on the substrate was swept out by heating to 1000 ℃ for 10 min in the growth chamber. A 30 nm

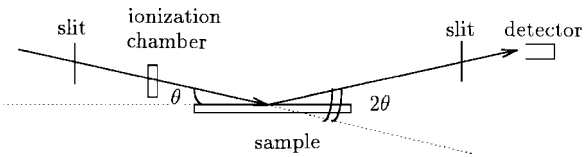

Fig.2. Layout of X-ray low angle reflection experiment.

thich Si buffer layer was first grown on the substrate at 600 ℃; then one monolayer of Sb atoms ($\sim 6.78 \times 10^{14}$ atoms/cm^2) was deposited at 300 ℃ on the buffer layer. The Si cap layer of 20–30 nm thickness was then grown on the Sb monolayer at a growth rate of 0.1 nm/s. The growth temperatures of the Si layers were selected to be 250, 300, 350 and 400 ℃ for different samples.

The low angle X-ray reflectivity measurements were carried out at the diffuse scattering station of the Beijing Synchrotron Radiation Facility.[11] The layout of the experiment is shown in Fig.2. A focused monochromatic X-ray beam ($\lambda = 0.154$ nm), obtained from the 4W1C beamline, passed through the entrance slit and was incident on the sample at an angle of θ and then reflected by the sample to the detector placed at 2θ. The sample and the detector were rotated together in synchronization to obtain X-ray reflectivity data at different incident angles.

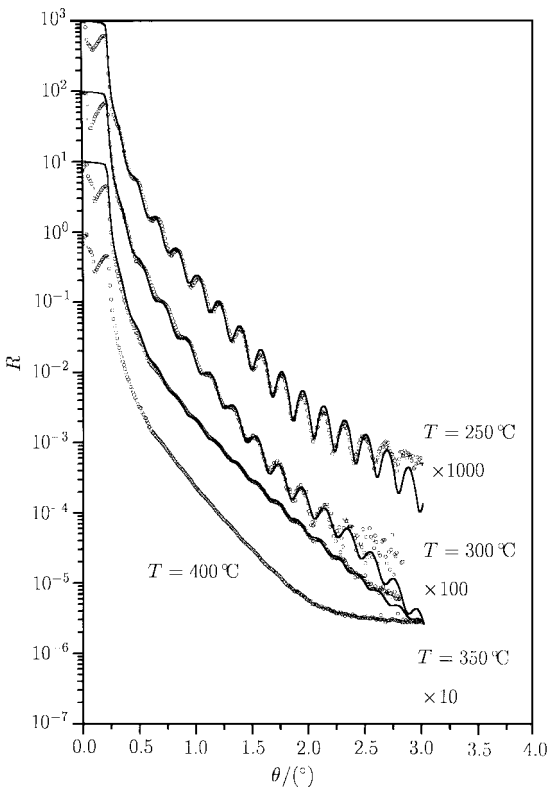

Fig.3. The experimental reflectivity curves (○) and simulated curves (—).

Because of the intense reflected X-rays near the total reflection angle, an absorption plate was used to avoid saturation of the NaI(Tl) detector in the region of $\theta = 0°$–$0.5°$. During the experiments, the electron energy of the storage ring was 2.2 GeV with a beam current of 70–30 mA which decayed with time. Therefore, a transmission ionization chamber was placed between the entrance slit and the same holder (Fig.2) to monitor the variance of the incident intensity to normalize the experimental data for the reflectivity.

The experimental reflectivity curves obtained for different samples are shown in Fig.3. The curves tend to slope downwards with increasing incident angles, but are accompanied by intensity oscillations which are caused by the dopant distribution. The reflectivity oscillations of the sample grown at 250 ℃ is very obvious, which indicates that the Sb atoms are strongly localised in the Si crystal to form a very narrow Sb-rich layer. From the period of the oscillations $\Delta\theta(\sim 0.185°)$ in the high angle region, the depth of the Sb-rich layer is obtained to be about 23.8 nm. For samples grown at higher temperatures, the amplitudes decrease gradually with increasing temperature. No oscillations have been observed on the reflectivity curve of the sample grown at 400 ℃, which indicates that there is no change of electron density caused by the dopants in the crystal. That is, most of the Sb atoms have segregated to the surface in the growth process, as discussed in section Ⅱ.

Ⅳ. SIMULATION AND DISCUSSION

The X-ray scattering of solid materials comes mainly from electrons in the atoms, so from the reflected X-ray intensity we can obtain information on the variation of electron density along the depth, which reflects the component distribution of these materials in the depth direction. For materials in which the electron density is distributed homogeneously, the X-ray reflectivity is satisfied by the Fresnel reflection formula; for those in which the electron density is inhomogeneous, we can divide the sample along the depth direction into several thin layers, so that the electron density in each thin layer may be considered to be constant. The reflectivity is then obtainable from the Parratt recursion[12] relationship.

The Parratt′s recurrence formula and the exponential model of Sb atom distribution in the Si crystal, as given in section Ⅱ, were employed to simulate the experimental reflectivity data. The main parameters used for simulation were the dopant depth d', the decay length τ, and the number of Sb atoms N'_d. The depth d' corresponds to the period of intensity oscillations on the reflectivity curve, while the number of Sb atoms N'_d and the decay lenght are strongly related to the amplitude and envelope of the oscillations.

Since the samples were kept in air after the growth, a SiO_2 surface layer of thickness d_s and also the surface roughness σ_s were included in the simulations. These two parameters influenced the trend of the reflectivity curves but not the modulations. The simulated curves which fitted best with the experimental curves are shown in Fig.3 and the parameters of the samples are listed in Table 1.

As shown in Fig.3, the simulated curves fit the experimental reflectivity curves very well, which indicates that the exponential distribution models obtained from the argument of Sb atom segregation depict the distribution of dopants exactly. The simulated Sb atomic distributions of those samples are shown in Fig.4. The Sb atoms were exponentially distri-

Table 1. Sample growth and simulation parameters. T: growth temperature of the Si cap layers; d, d': nominal and simulated depths of the Sb monolayer; N_d, N'_d: nominal and simulated number of doped Sb atoms in units of monolayers; τ: 1/e decay length of the Sb atomic distribution; d_s: thickness of the SiO_2 layer on the surface; σ_s: surface roughness.

T/℃	d/nm	d'/nm	N_d	N'_d	τ/nm	d_s/nm	σ_s/nm
250	25.0	23.7	1	0.9	0.45	2.3	0.39
300	20.0	21.6	1	0.9	0.95	2.5	0.5
350	25.0	24.5	1	0.9	3.5	1.6	0.33
400	30.0	-----	1	-----	-----	-----	-----

buted in the Si crystal with a 1/e decay length of 0.45, 0.95 and 3.5 nm for samples grown at 250, 300 and 350 ℃, respectively. Similar exponential distributions of dopant atoms were also observed by Slijikerman *et al.* in solid epitaxial Si layers, while the Gaussian distribution of dopant atoms was observed by Xiu *et al.* The different distributions obtained must be caused by the difference in their sample preparations. Slijikerman *et al.* deposited the Sb layer on Si crystal substrate and then the cap layer of amorphous Si on the Sb layer. During the heat treatment at 800 K to crystallise the amorphous Si, the diffusion coefficients for Sb diffusing to crystalline and to amorphous Si were very different (very difficult for the former but easy for the latter), so that the Sb atomic distribution became asymmetric, similar to the case of Fig.4. However, in the solid phase growth process employed by Xiu *et al.*, both sides of the Sb monolayer were amorphous Si. There was no preference for the Sb atoms to diffuse into either side during high temperature Si crystallisation, so that a symmetric Gaussian distribution of Sb atoms was then formed.

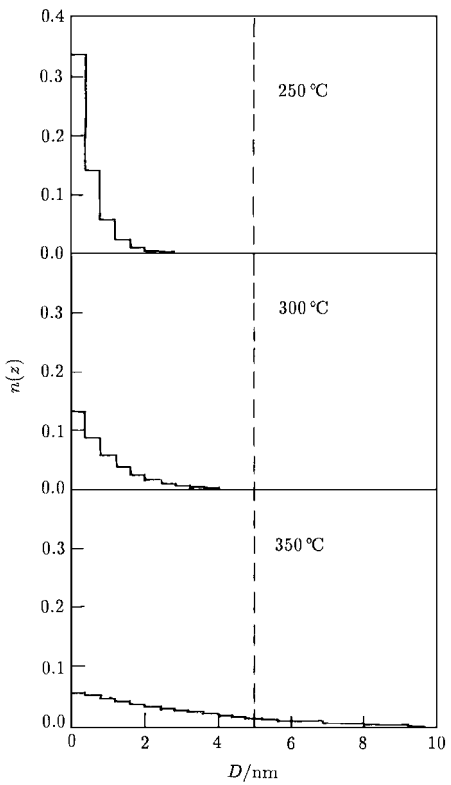

Fig.4. Simulated Sb atomic distribution in the Si epitaxial layers. The zero layer is located at $D = 0$ as seen in Fig.1. The dashed line at 5 nm illustrates the range of δ-doping spreading.

During the sample preparation, the Sb monolayers were deposited at 300 ℃ in excess, to ensure that the number of Sb atoms was the same in different samples. From Table 1, this saturated surface density of Sb atoms was determined to be 0.9 ML, which is consistent with the reported value of 0.8–1.0 ML.[13,14]

It is commonly recognised that δ-doping is only realized when the spreading range of the dopants is less than to 5 nm. Accordingly, as we see from the data of Table 1 and Fig.4, only the samples grown at temperatures below 300 ℃ are δ-doped. In the sample prepared at 350 ℃, quite a fraction of the Sb atoms are spread over a region greater than 5 nm. For the

sample grown at 400 ℃, no oscillations are observed on the reflectivity curve. This indicates that most of the Sb atoms have segregated to the surface.

This conclusion is different from the results of Jorke which were extrapolated from experiments.[14] According to the extrapolated curve of Ref.[4], the segregation of Sb atoms in the Si crystal would be quite weak at temperatures below 400 ℃. Since their argument is based on the extrapolation of experiments at temperatures higher than 400 ℃, and with many fewer Sb dopant atoms, it may be different for samples with much higher dopant content grown at 400 ℃. Our results show that for an Sb surface density of about 1 ML, the segregation of Sb atoms is very strong at 400 ℃, so only temperatures below 300 ℃ are suitable for the δ-doping of Sb atoms in Si crystal by MBE.

V. CONCLUSION

With the help of bright synchrotron radiation X-rays, the distributions of δ-doped Sb atoms in Si crystal were successfully measured from the X-ray reflection. The segregation of Sb atoms at different temperatures was then studied according to the Sb atomic distributions. Our results show that temperatures below 300 ℃ are necessary for the δ-doping of Sb atoms in Si crystal by MBE to limit the distribution depth of the Sb atoms to less than 5 nm. At 400 ℃ the segregation of Sb atoms is too strong to realise the δ-doping of Sb in Si crystal.

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