Strain analysis of InP/InGaAsP wafer bonded on Si by X-ray double crystalline diffraction

Hong-Quan Zhao ∗, Li-Juan Yu, Yong-Zhen Huang, Yu-Tian Wang

State Key Laboratory for Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China

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Abstract

Wafer bonding between p-Si and an n-InP-based InGaAsP multiple quantum well (MQW) wafer was achieved by a direct wafer bonding method. In order to investigate the strain at different annealing temperatures, four pre-bonded pairs were selected, and pair one was annealed at 150 °C, pair two at 250 °C, pair three at 350 °C, and pair four at 450 °C, respectively. The macroscopical strains on the bonded epitaxial layer include two parts, namely the internal strain and the strain caused by the mismatching of the crystalline orientation between InP (1 0 0) and Si (1 0 0). These strains were measured by the X-ray double crystalline diffraction, and theoretical calculations of the longitudinal and perpendicular thermal strains at different annealing temperatures were calculated using the bi-metal thermostats model, both the internal strain and the thermal strain increase with the annealing temperature. Normal thermal stress and the elastic biaxial thermal strain energy were also calculated using this model.

Keywords: InP; Si; X-ray double crystalline diffraction; Thermal strain; Wafer bonding

1. Introduction

Over the past 10 years, direct wafer bonding has received considerable attention for releasing the restrictions of lattice matching imposed by epitaxial growth and opening new degrees of freedom for the design of semiconductor devices [1–10]. During the wafer bonding process, thermal treatment is a very important step, which increases the surface energy and bonding strength of the bonded wafers [11]. However, if the bonded materials have different expansion coefficients, thermal strain will develop in the course of annealing and cooling. Furthermore, a big internal strain will severely affect the bonding quality and induce a high density of dislocations [12–14], even result in the failure to bond [15]. Therefore, it is important to study the strain of bonded wafers and the distribution of stresses, and to put forward an effective method to reduce these stresses.

2. Wafer bonding process

Single-facet polished silicon and InP wafers were used in this work. The 2-inch p-type silicon wafers were standard bare CZ-grown (1 0 0) orientation wafers, with a thickness of 280 μm, resistance of 1–50 Ω cm, and a surface root-mean-square (RMS) roughness ≤0.3 nm. A laser structured wafer with six InP/InGaAsP quantum wells, and with an epitaxial layer of about 4 μm was grown on a 380-μm-thick InP (1 0 0) substrate by MOCVD and used for wafer bonding.

The wafer bonding process is summarized as follows. The hydrophilic-treated InP and Si wafers were pre-bonded and baked at 70 °C for 5 h to drive the water out in order to prevent blisters in the subsequent annealing steps. The annealing process has three steps. First, the pairs bonded by the van der Waals force were put into a vacuum stove with a pressure of 40 N/cm² on the wafer pairs, and annealed in a vacuum at a slow temperature-rising rate (0.1 °C/min). When it reached 150 °C, 5 h of constant-temperature annealing was performed on the pairs. After that, the annealing temperature descended to 20 °C at a rate of ~0.1 °C/min. Second, the InP substrate of the bonded pairs was mechanically thinned to about 150 μm. Third, the four bonded pairs were further annealed separately in a vacuum without any pressure on the pairs. Pair one was annealed at 150 °C again as the first step did. Pair two was annealed at a slow temperature rising rate of 0.1 °C/min when it reached 150°C, 5 h of constant-temperature annealing was performed to the pair. Subsequently, the temperature continued to increase at a rate of 0.3 °C/min. As it reached 250 °C,
Fig. 1. The deflection of X-ray 2θ diffraction angle induced by internal strain and the strain caused by the mismatching of the crystalline orientation between InP (1 0 0) and Si (1 0 0). Samples were annealed at (a) 150 °C, (b) 250 °C, (c) 350 °C, (d) 450 °C. The dashed line labeled “bonded InP” indicates the measured diffraction angle with the X-ray incident angle of 31.667° irradiated on bonded InP transferred layer; the thin solid line labeled “bonded InP” indicates the measured diffraction angle with the X-ray incident angle of −31.667° irradiated on the bonded InP transferred layer; the thick solid line labeled “unbonded InP” indicates the Bragg diffraction angle 2θ of the stress-free InP.

5 h of constant-temperature annealing was performed to the pair. Finally the annealing temperature descended to 20 °C at a rate of −0.3 °C/min. Pair three was first annealed with a temperature-rising rate of 0.1 °C/min, and then be constant-temperature annealed at 150 °C for 5 h. After that, the annealing temperature continued to increase at a rate of 0.3 °C/min. As it reached 250 °C, the pair was constant-temperature annealed for 5 h. Then the annealing temperature continued to increase at a rate of 0.5 °C/min, as it reached 350 °C, constant-temperature annealing was performed to the wafer for 2 h. Finally, the annealing temperature increased to a rate of 1 °C/min. As it reached 450 °C, the pair was annealed for 30 min. Finally, the annealing temperature descended to the room temperature at a rate of −1 °C/min. As the annealing temperature increases, the temperature rises or descends more quickly, and the time for constant-temperature annealing is also reduced. This will increase the internal stress. The InP substrates on the bonded pairs were finally removed by selective wet chemical etching, leaving only the 4-μm-thick epitaxial layer on the Si substrate. The etching solution is hydrochloric acid: H2O = 4:1 at 20 °C.

3. Strain measurement by X-ray double crystalline diffraction

The strains of the bonded pairs prepared by the method described above were then measured by a RIGAKU-SLX-1A X-ray double crystalline diffraction instrument. Since the Bragg diffraction angle θ of InP single crystal is 31.667°, we select ±31.667° as the two X-ray incident angles for investigating the strain. Most of the strain is loaded on the 4-μm-thick epitaxial layer since the InP substrate has been removed. The strain of the bonded wafer consist of two parts, namely the internal strain εi and the strain caused by the mismatching of the crystalline orientation between InP (1 0 0) and Si (1 0 0) εδ. Fig. 1(a)–(d) show the X-ray double crystalline diffraction spectra of the four bonded wafers. The Bragg diffraction angle 2θ of strain-free InP is 63.334°. When the 31.667° incident X-ray beam is irradiated on the bonded wafer, the diffraction angle is 2θ + Δ2θ + δ,
and when it is changed to $-31.667^\circ$, the diffraction angle is $2\theta - \Delta 2\theta + \delta$. Then the offset $\Delta \theta$ of the diffraction angle caused by the internal stress, and the mismatching $\delta$ of the crystalline orientation between InP (1 0 0) and Si (1 0 0) can be calculated [16].

The internal strain can be expressed as follows:

$$\varepsilon_i = \frac{d_n - d_0}{d_0} = \frac{\Delta d}{d} = \cot \theta_0 \times \Delta \theta \tag{1}$$

The strain caused by the deflection of the crystalline orientation is

$$\varepsilon_\beta = \frac{d_n' - d_0}{d_0} = \frac{\Delta d'}{d_0} = \cot \theta_0 \times \delta \tag{2}$$

where $d_0$ is the non-straining InP (1 0 0) facet spacing, $d_n$ is the internal-straining InP (1 0 0) facet spacing, and $d_n'$ is the straining (induced by the crystalline orientation mismatching) InP (1 0 0) facet spacing.

The internal stress is the force which induces moment in the bonded film. When the internal stress is bigger than the high-point of the elastic deformation of the bonded film that can bear, the bonded film will peel off. The internal stress of the bonded film is constituted of two parts, namely the thermal stress and the intrinsic stress, which can be expressed as [17]:

$$\sigma_i = \sigma_{th} + \sigma_{in}$$

The stresses that we measured in the experiments are the mixture of the thermal stress and the intrinsic stress, and in many conditions, the intrinsic stress is deemed the main part [17]. The thermal strain is related with the difference of the thermal expansion coefficients between the bonded film and the Si substrate. Besides the thermal stress, Buckel [18] has investigated six sources of the intrinsic stress, these sources are all exist during the wafer bonding process, and which can be concluded as:

1. The combination of the atoms between the bonded film and the substrate, for example the existence of the residue of gases such as oxygen and hydrosphere and the chemical reaction in the bonding interface will be one source of intrinsic stress [19–20].

2. The difference of the lattice space between the bonded film and the substrate is another source for the intrinsic stress. If the bonded film is thick enough or the lattice mismatch between the bonded film and the substrate is high, the strain energy in the bonded film will be released through the rearrangement of the interface dislocation and defects, and to decrease the whole energy of the bonded system. This interface dislocation rearrangement mechanism is strongly related with the origin of the intrinsic stress [21–23].

3. When the temperature of the thermal treatment is high enough (above 350 °C), the indium in the InP surface will separated out to the bonding interface [24]. The indium atoms first form islets in the InP/Si interface, as the islets grow up, the combination strength between the indium islets and the InP and Si basal body is strengthened, the movement of these atoms are restricted by the basal body. At the same time, the crystallization of the islet is suppressed by the interfacial force, and the compression stress produced. As the augmentation of the islet, the attractive force augmented because of the reducing of the distance among these islets, and then tension stress produced [25–27].

4. Intensive stress also produces in the course of the recrystallization process of the separated indium islets. There are several different models to simulate the production mechanism of the stress [28–29].

5. The particular arrangement of the micro-cavities, defects and dislocations in the bonding interface will induce intensive stress [30–31].

6. Intensive stress also produces during the phase transformation of the chemical reaction process in the bonding interface [18].

Because the penetration depth of X-ray is about 10 µm, the surface of the bonded film can be considered as a free surface. Considering an arbitrary point on the surface of the bonded film, as it is a free surface, then the stress which is perpendicular to the surface is zero. The stress state is transformed to the two-dimensional stress state [16]. There are three normal stresses $\sigma_1$, $\sigma_2$ and $\sigma_3$, the normal stresses $\sigma_1$ and $\sigma_2$, which have the same value, are parallel to the plane, and $\sigma_3$, which is zero, is perpendicular to the InP (1 0 0) facet. The strain $\varepsilon_3$, which is caused by the mismatching of the crystalline orientation between InP (1 0 0) and Si (1 0 0) will induce no stress. When the materials are isotropic, the internal strain $\varepsilon_1$, which is perpendicular to the plane, can be expressed as [16]

$$\varepsilon_1 = \frac{d_n - d_0}{d_0} = -\nu(\varepsilon_1 + \varepsilon_2) = -\frac{\nu}{E}(\sigma_1 + \sigma_2) \tag{3}$$

We calculated the strain and the stress by applying these equations and the results are listed in Table 1. Young’s modulus $6.11 \times 10^{10}$ N/m$^2$ and $1.3 \times 10^{11}$ N/m$^2$, Poisson’s ratios 0.36 and 0.28, and thermal expansion coefficients $4.8 \times 10^{-6}$/K and

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The offset of diffraction angle and corresponding strain and the normal stress calculated from the X-ray double crystalline diffraction results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anneling temperature</td>
<td>$\Delta \theta$ (degree)</td>
</tr>
<tr>
<td>150 °C</td>
<td>0.078</td>
</tr>
<tr>
<td>250 °C</td>
<td>0.135</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.158</td>
</tr>
<tr>
<td>450 °C</td>
<td>0.228</td>
</tr>
</tbody>
</table>
2.6 × 10⁻⁶/K are used for InP (1 0 0) and Si (1 0 0), respectively [32], and the parameters are assumed to be independent of temperature.

4. Thermal analysis of circular bonding wafers with a bi-metal thermostat model [33,34]

Thermal strain was calculated as a function of distance from the center to the edge and the thickness of InP wafer with a bi-metal thermostat model. Fig. 2 shows a schematic of this model. Circular bonding wafers were analyzed at different annealing temperatures from 150 °C to 550 °C.

Before the calculation, there are three scenarios to be taken into account. First, we assume that the bonding is strong enough already at room temperature, that no sliding or plastic deformation in the transferred layer would occur during the heating. Thus there should be no thermal stress at all after returning to room temperature. Any observed stresses must be associated with not getting an ideally flat surface or with the mismatching of the crystalline orientation between the two wafers. However, the wafers used in the experiment were so flat that their RMS roughness was <0.3 nm, and the strain caused by the mismatching of the crystalline orientation between the two bonding wafers was also very small compared with the total strain that we measured by X-ray double crystalline diffraction. Based on this reason, the strains caused by the differences of thermal expansion coefficients between the two wafers of InP and Si should be taken into account.

Second, we assumed that the InP and Si wafers were bonded by van der Waals forces during the room temperature process. According to Tong and G¨osele [35], if hydrogen bonding can be realized across two mating surfaces, it will result in strong dipole-dipole van der Waals attraction forces between these surfaces. Moreover, when the mating surfaces are hydrophilic and water molecules are present, the linkages of two or three water molecules may bridge the gaps between the two mating surfaces. As the annealing temperature rises, the water molecules are volatilized gradually and the bonding interface is mainly bridged by In—O—Si bonds at a comparatively high temperature (generally above 400 °C) [36,37]. The number of In—O—Si bonds increases as the annealing temperature rises. However, the surface oxide still has a few isolated OH groups of 0.06OH/100Å² even after annealing at 1100 °C [35]. The size of an —OH group is 1.01Å [35], and the distance between two hydrogen–bonded oxygen atoms in ice is 2.76Å [35]. When the radius of the wafers is 1cm, the relative displacement of the mating wafers is about 220Å as the temperature increases by 1 K, according to the thermal expansion coefficients of InP and Si. Therefore, we can assume that as the temperature increases, the primary weak hydrogen bonds rupture, and the wafers slide against each other. When a balance is reached, a strong bond between the two mating surfaces is formed. Thermal stresses are generated and then relax as the temperature increases in a quasi-static state at a rate of about 0.1–0.5 °C/min. As the temperature peaks, the strongest bonds are formed during the constant temperature treatment process; the generating and relaxing of the thermal stresses reach a dynamic balance. Later, as it cooled to the room temperature in a quasi-static state at a rate of about 0.1–0.5 °C/min, the maximum value of thermal strain develops in the transferred layer. This assumption is close to the direct wafer bonding mechanism.

Based on the second assumption, we have made another relatively simple assumption in order to apply the bi-metal thermostat model [38] to the thermal stress analysis of the direct wafer bonding. We assumed that the bonding at room temperature is weak enough that the two wafers can slide against each other, and bonding strong enough to prevent sliding develops only after the highest constant temperature thermal treatment process. As it cools down, thermal stresses developed. This assumption ignores the dynamic process of the generation and relaxation of the thermal stresses, supposing that the thermal stresses are only related to the highest annealing temperature. This assumption will inevitably induce a bigger value of calculated thermal stresses than the real one. During the computation, we assume that all physical parameters are independent of temperature, and no bubbles, de-bonding, sliding, or structural or compositional changes occur during temperature changes; Young’s modulus, Poisson’s ratio, and the thermal expansion coefficients are linear, elastic, and isotropic.

The normal stress (parallel to the interface) on the InP layer is maximum at the interface, and its lateral distribution σ(x) at the interface of the InP wafer is given by [39]:

\[ \sigma(x) = 10^{-6} \times \frac{\Delta \alpha \Delta T}{\lambda t_{w1}} \left[ 1 + \frac{3t_{w1}D_1}{t_{w1}D} \right] \left[ 1 - \exp[-K(R - x)] \right] \]  

(4)

where x is the distance from the center to the edge at the interface, \( \Delta \alpha = \alpha_2 - \alpha_1 \) is the difference between the thermal expansion coefficients of InP (1 0 0) and Si (1 0 0), \( \Delta T \) is the temperature change, \( t_w = t_{w1} + t_{w2} \) is the thickness of the whole bonded pair, and

\[ \lambda = \left( \frac{1 - v_1^2}{E_{1t_{w1}}} + \frac{1 - v_2^2}{E_{2t_{w2}}} + \frac{3(t_{w1} + t_{w2})^2(1 - v_1^2)(1 - v_2^2)}{E_{1t_{w1}}(1 - v_1^2) + E_{2t_{w2}}(1 - v_2^2)} \right) \]  

(5)

\[ D_1 = \frac{E_{1t_{w1}}^3}{12(1 - v_1^2)} \]  

(6)
\[ D_2 = \frac{E_1 t_{w2}^3}{12(1-\nu^2)} \] (7)

\[ D = D_1 + D_2 \] (8)

The vertical distribution of the normal stresses within the InP wafer at the center of the wafer can be expressed as

\[ \sigma(y) = 10^{-6} \times \frac{1}{\rho} \left[ (y-t_{w1}) E_1' - \frac{2}{t_{w1}(t_{w1}+t_{w2})} \times \left( \frac{E_1' t_{w1}^3 + E_2' t_{w2}^3}{12} \right) \right] \] (9)

where \( y \) is the distance measured from the bonding interface of the bonded pair, \( E' = E/(1-\nu) \) is the biaxial modulus, and \( \rho \) is the radius of curvature of the bonded pair which can be expressed as

\[ \rho = \frac{(E_1' t_{w1}^3 + E_2' t_{w2}^3) (E_1' t_{w1} + E_2' t_{w2}) + 3E_1' E_2' t_{w1} t_{w2} (t_{w1} + t_{w2})^2}{6E_1' E_2' t_{w1} t_{w2} (t_{w1} + t_{w2}) \Delta T} \] (10)

Then the strain which is parallel to the surface on the epilayer \( \varepsilon_x \) caused by the thermal stress can be expressed as follows:

\[ \varepsilon_x = \int_0^x \left[ \frac{\sigma_x - \nu(\sigma_y + \sigma_z)}{E_1} + \alpha_{\text{InP}} \Delta T \right] \, d\xi \] (11)

As the material is cubic lattice simple crystal, the strain which is perpendicular to the surface can be calculated by expression (3).

The specific elastic biaxial strain energy (unit area elastic energy) \( E_{el} \) from pure bending in the InP layer is approximately given by [35]:

\[ E_{el} = \int_0^{t_{w1}} \frac{\sigma_1^2(y)}{2E_1} \, d\xi \] (12)

Fig. 3 shows the thermal strain perpendicular to the surface at the bonding interface calculated by the bi-metal thermostat model and the internal strain which is perpendicular to the surface measured by the X-ray double crystalline diffraction varies with the annealing temperature. From Fig. 3 we can see that thermal strain is much smaller than the corresponding measured internal strain, but their variational trend with the annealing temperature is similar, this also indicate that the thermal strain is only one part of the internal strain, and both of the two strains are increase with the annealing temperature.

Fig. 4(a) and (b) show the thermal strain on the \( x \)-direction on the bonded InP layers which were annealed at different temperatures from 150 °C to 550 °C, as it varies with the distance from the center to the edge and the thickness of the InP layer. From Fig. 4 we can see that thermal strain which is parallel to the surface increases linearly as it approaches the edge of the interface. Thinning the InP substrate to an appropriate thickness (about 150 μm) before annealing can decrease the thermal strain.

Fig. 5 shows the normal thermal stress on the bonded InP layer as it varies with (a) the distance from the center to the edge, and (b) the thickness of the InP layer at different annealing temperatures from 150 °C to 550 °C. The calculated thermal stress is also smaller than the measured corresponding internal stress in Table 1. We think the cause is that the thermal stress...
is only one small part of the internal stress. The normal thermal stress decreases exponentially as it approaches the edge of the interface, and thinning the InP substrate to an appropriate thickness (about 150 μm) before annealing can decrease the normal stress effectively.

Fig. 6 shows the elastic biaxial strain energy in the InP layer as it varies with thickness of the InP substrate at different annealing temperatures. The elastic energy changes drastically as the thickness of the InP wafer varies. When thinned to about 150 μm, before annealing, the elastic biaxial strain energy decreases to an infinitesimal value.

5. Conclusion

InP (100)-based InP/InGaAsP multi-quantum well epitaxial layers were transferred onto Si (100) by a direct wafer bonding and selective wet chemical etching. X-ray double crystalline diffraction was applied to investigate the internal strain, and the strain caused by the mismatching of the crystalline orientation between InP (100) and Si (100) in the bonded pairs. Thermal strain both in the planar and perpendicular direction, and normal thermal stress which is parallel to the surface, and the elastic bi-axial strain energy of the InP-Si bonded pairs at different annealing temperatures from 150 °C to 550 °C were calculated with a bi-metal thermostat model. The calculated values are smaller than the corresponding measured value, this indicates the internal strain and stress is much bigger than the corresponding thermal strain and stress, there are many other factors that cause strain and stress in the bonded pairs. The calculated results also tell us that when the thickness of the Si wafer is fixed at 280 μm (commercially available), the thermal strain and the normal stress and the elastic bi-axial strain energy can be effectively decreased by thinning the InP substrate to about 150 μm before annealing.

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