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Studies on growth mechanism of HgCdTe epilayer on Si grown by HWE

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In this paper, the mechanism of $Hg_{1-x}Cd_xTe$/Si heterojunction grown by HWE (Hot Well Epitaxy) was studied. Opitical characterizations were shown with FTIR, the composition $x = 0.39$ was deduced by using MIR transmittance, the absorbing peak at 319.4 cm^{-1} was measured by FIR transmittance, 319.4 cm^{-1} confirmed the existence of Si–Te bond of at Si/HgCdTe interfacial layer. The I-V characteristics at both room temperature and 77 K of HgCdTe (*n*-type)/Si (*p*-type) heterojunction show that the good p-n heterojunction properties was obtained by using HWE. XRD study confirmed the formation of (111) oriented HgCdTe on (211) Si. Morphology of a cross section observed using EPMA indicates the columnar growth of HgCdTe. An analysis of interfcial layer by EPMA indicated presence of three layers composed of Si + Te, Si + Te + Hg and Si + Te + Cd + Hg. Among them, the most important one is the first layer. The problem of lattice mismatch and the difference of thermal expansion coefficient between Si and CdTe or HgTe may be improved by formation of Si–Te stable chemical bond through bybridization orbital bonding between Si and Te. The second and third layers are formed by evaporation-interdiffusion. Formation of the whole interfacial layer provides the appetency for the growth of (111) $Hg_{1-x}Cd_xTe$ epilayer on (211) Si substrate. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

$Hg_{1-x}Cd_xTe$ is a kind of ternary alloy semiconductor materials, which composed of the semiconductor CdTe and the semimetal HgTe. IR detector developed from $Hg_{1-x}Cd_xTe$ may be used for 1–3 μm, 3–5 μm, and 8–14 μm atmospheric windows, resulting in its wide use in fields of aviation, space etc.

HgCdTe may grow on a variety of substrates, such as GaAs, sapphire, and Si etc., among them, Si substrate has the following advantages, large area, low cost, and high rigidity, Si substrates transparency up to far infrared allowing the back side illumination for the second atmospheric window, or longer wavelength devices. Especially for the real integrated signal processing chip was allowed by growing $Hg_{1-x}Cd_xTe$ film on electrically active silicon substrates [1]. However, since Si is diamond structure and HgCdTe is the cubic zincblende structure, and the big lattice mismatch (about 20%) and difference in thermal expansion coefficients (more than a factor of 2) [2]. The growth of HgCdTe on Si substrate is difficult, to solve this problem, this paper arms to grow HgCdTe/Si heterojunction by HWE and discuss the mechanism for formation of heterojunction.

2. Experimental

2.1. Growth of HgCdTe thin film on Si substrate by HWE

Using refitted HWE oven to grow HgCdTe thin film, the detailed technics is illustrated as follows: *p*-type (211)

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Si substrate with a 300 μm thickness was rinsed by trichloroethylene and hydrochloric acid, respectively, followed by polishing, then, rinsed by hydrofluoric acid. To avoid contamination, deioned water was used to clean the rudimental regents after using each regent. Clean Si substrate can be obtained after being treated with above procedures, the rinsed Si substrate was put into vacuum system, temperature was increased to 900°C to deoxidize Si substrate. The deoxidized Substrate was passivated by opening Te flux after decreasing temperature to 550°C. CdTe was grown to 100 nm on Si substrate at 250°C, annealed at 350°C for a while, grown again to 4–8 μm at 300°C, then the substitute CdTe/Si substrate is obtained. The substrate was taken out from the vacuum system and eroded away 300–500 nm by Br_2/ethanol solution. HgTe source was rinsed by double distilled water, then put into growth chamber. At 560–650°C, the composition x of $Hg_{1-x}Cd_xTe$ was adjusted by means of changing inner Hg pressure and growth temperature. After ~8 h of growth, HgCdTe thin film with ~25 μm thickness and a diameter $\Phi \geq 30$ mm can be gotten. Then, HgCdTe thin film was annealed at 400–350°C to convert conduction type, experimental temperature was decreased to room temperature, p-type HgCdTe thin film was grown.

2.2. FTIR characterization

The middle IR (MIR) characterization for $Hg_{1-x}Cd_xTe$/Si heterojunction was completed by FTS-40 FTIR (BIO-RAD), the testing conditions were as follows, scanning coverage = 4000–400 cm^{-1}, RES = 8 cm^{-1}, SCANS = 16.

The far IR (FIR) characterization for $Hg_{1-x}Cd_xTe$/Si heterojunction was performed by 1760X FTIR (PE), the testing conditions were as follows, scanning coverage = 500–50 cm^{-1}, RES = 8 cm^{-1}, SCANS = 16.

Both MIR and FIR characterizations were performed at room temperature.

2.3. I-V characterization

The I-V characteristics of In-HgCdTe(n-type)/Si(p-type)-In heterojunction were characterized by using KEITHLEY 82DOS. The testing conditions were as follows, "+" In-HgCdTe(n-type)/Si(p-type)-In voltage scanning,"−"In-HgCdTe(n-type)/Si(p-type)-In voltage scanning at both room temperature and 77 K.

2.4. XRD characterization

The HgCdTe epilayer was characterized by D/Max-3B X-ray diffractometer under the following conditions; Cu target ($\lambda = 1.5406$ Å), 40 kV, 30 mA, DS = SS = 1°C, RS = 0.3 mm, graphite monochromator, scanning speed = 10°min^{-1}, scanning coverage = 0–100° (with a $\leq \pm 0.01°$ precision), the XRD characterization was completed at room temperature.

2.5. EPMA characterization

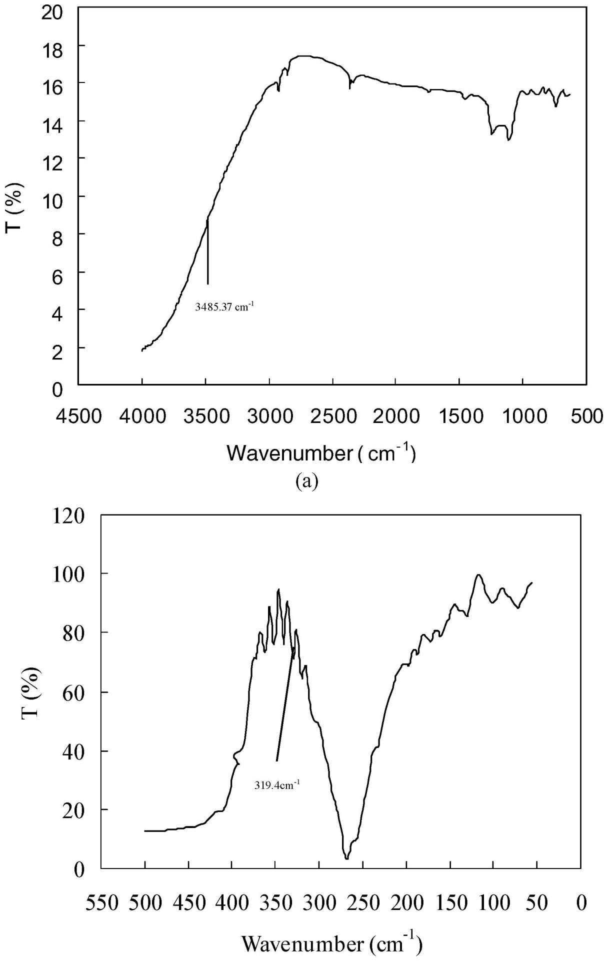
The cross section morphology of HgCdTe/Si heterojunction and the distribution of the four elements Si, Te, Cd, Hg have been characterized by EPMA-1600 type electronic probe under the conditions that, accelerating voltage = 30 kV, sample current = 50 nA, and using ADP and LiF crystals, the EPMA characterization was carried out at room temperature.

3. Results and discussion

3.1. FTIR characterization

Fig. 1a is the middle IR (4000 – 400 cm^{-1}) transmission spectrum of HgCdTe/Si heterojuncture, the composition x of $Hg_{1-x}Cd_xTe$ was calculated from the cut off wavelength (3485.37 cm^{-1}), which equals the wavelength corresponding to 50% of the maximum transmission percent. Using Schmit's equation, the composition of $Hg_{1-x}Cd_xTe$ was calculated ($x = 0.31$).

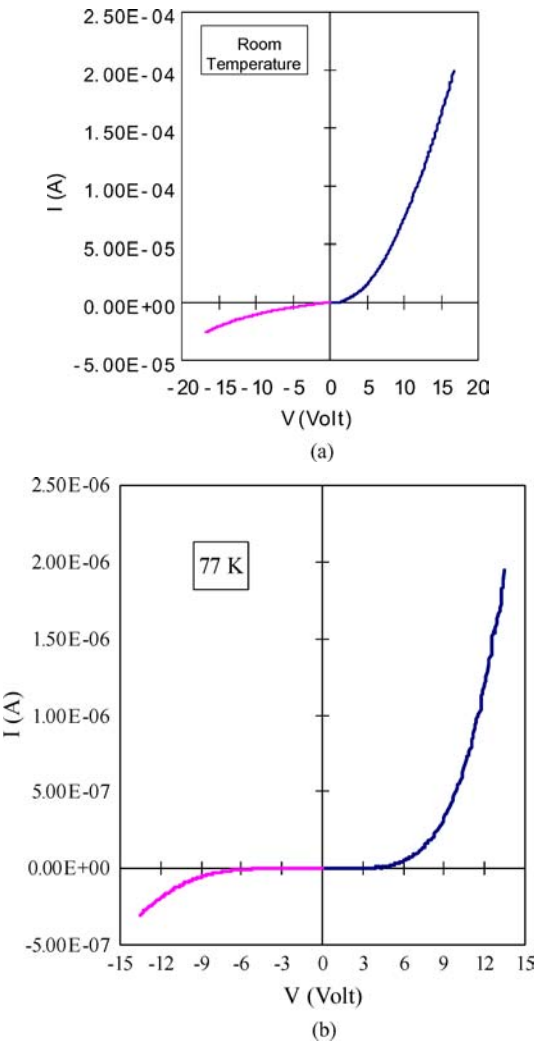
Fig. 1b is the far IR (500–50 cm^{-1}) transmission spectrum of HgCdTe/Si heterojuncture, the tested peak 319.4 cm^{-1} is attributed to the vibrational peak of Si–Te. According to the Hilton's conclusion: The absorption for Si–Te is caused by the linearly symmetric stretch of XY_2 molecule, 322 cm^{-1} is the basic



(a)

(b)

Figure 1 (a) The MIR transmission spectrum of $Hg_{0.61}Cd_{0.39}Te$/Si heterojunction at room temperature. (b) The FIR transmission spectrum of $Hg_{0.61}Cd_{0.39}Te$/Si heterojunction at room temperature.



(a)

(b)

Figure 2 (a) The I-V characteristic of In-HgCdTe(*n*-type)/Si(*p*-type)-In heterojunction at room temperature. (b) The I-V characteristic of In-HgCdTe(*n*-type)/Si(*p*-type)-In heterojunction at 77 K.

absorption peak of Si–Te [3]. There is a small difference (2.6 cm^{-1}) between 322 cm^{-1} and 319.4 cm^{-1}, the difference is in the error range, for a testing condition is the resolution = 8 $\text{cm}^{-1.}$

3.2. I-V characterization

Fig. 2a and b are the I-V characteristics of In-HgCdTe(*n*-type)/Si(*p*-type)-In heterojunction at room temperature and liquid nitrogen temperature (77 K). Obviously, a good pn junction was obtained by the authors' HWE method, which plays an important role in application of HgCdTe solid thin film in photoelectric devices.

3.3. Study on HgCdTe solid thin film by XRD

Fig. 3 is the XRD pattern of the HgCdTe/Si heterojunction. According to the PDF (150770) [4], searched by computer, the three strongest peaks are (111), (220), and (311), showing that (111) oriented cubic CdTe exists in the heterojunction. According to PDF (320665) [4], the three strongest peaks of HgTe are (111), (220) and (311), indicating that the (111) oriented HgTe exists in the heterojunction, too. Compared PDF (150770) with PDF (320665), (111) CdTe is different from (111) HgTe, although the three strongest peaks for judging (111) CdTe and (111) HgTe are peaks $1^{\#}$, $5^{\#}$ and $7^{\#}$. Except for the three strongest peaks, the intensity for the remainder peaks are different. Anther distinct difference is that: CdTe contains (531), peak $16^{\#}$ (d = 1.093). As for HgTe, it contains (200), peak 2# (d = 3.234). It is well known that HgCdTe is the complex compound composed by semiconductor CdTe and semimetal HgTe, thus, the existence of HgCdTe can be confirmed by the presence of CdTe crystal and HgTe crystal.

3.4. Characterization of the cross section for HgCdTe/Si heterojunction

Fig. 4a is the photograph of the cross section for HgCdTe/Si heterojunction (×2000) observed by EPMA. It is clear that the growth of HgCdTe epilayer on the Si substrate presents the column-like growth.

Fig. 4b is the distribution diagram for elements Si, Te, Cd and Hg in the cross section of HgCdTe/Si heterojunction, they are Si+Te, Si+Te+Hg, Si+Te+Cd+Hg, Te+Cd, Te+Hg, Te+Cd+Hg, Te and Si, respectively.

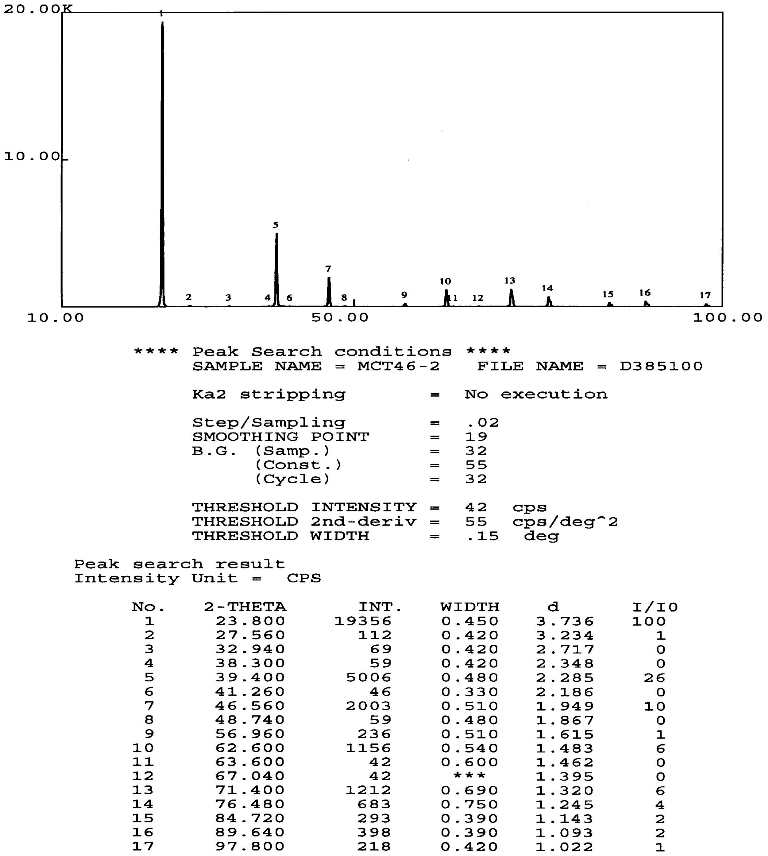
3.5. The mechanism for the formation of Si/HgCdTe interfacial layer

Fig. 4a shows that the growth of HgCdTe on Si substrate presents the column-like growth. Fig. 4b indicates that the growth of HgCdTe on Si substrate with the big lattice constant and thermal expansion coefficient mismatches. The successful preparation of HgCdTe/Si heterojunction is attributed to the growth of buffer layer(interfacial layer) with a thickness of 8.574 μm (the color band composed by pink, red and deep blue in Fig. 4b), these colors represent the distribution of the main elements Si+Te, Si + Te + Hg, and Si+Te+Cd+Hg.

According to the above information, we can deduce that the mechanism of forming the interfacial layer is:

3.5.1. Formation of Si + Te

Si has the diamond structure, which is formed by displacement of 1/4 length for the two faced cubic Brarais primitive cells along their diagonal. In diamond structure, every Si atom performs SP^3 hybridization with the other four Si atoms around it to form covalent bond, one Si atom is located in the center of the tetrahedron, the other four Si atoms are located at the four corners of the tetrahedron. Si is the element in IV A group, its valences are +4 and −4. Te is the element in VI A group, its main valences are −2 and +4. (211) oriented Si surface is composed by the (111) oriented platform, which only owns a single dangling bond [5]. The Si surface is the place for the terminator of periodic potential field, therefore, the less symmetrical property and the remnant band force are the driving force for the surface adsorption. In vacuum chamber, using hydrogen to passivate the Si surface. Te has been provided after hydrogen desorbed from the passivated



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**** Peak Search conditions ****
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     Step/Sampling         =  .02
     SMOOTHING POINT       =  19
     B.G.  (Samp.)         =  32
           (Const.)        =  55
           (Cycle)         =  32

     THRESHOLD INTENSITY =  42   cps
     THRESHOLD 2nd-deriv =  55   cps/deg^2
     THRESHOLD WIDTH     =  .15   deg

Peak search result
Intensity Unit =   CPS

     No.    2-THETA      INT.    WIDTH      d       I/IO
      1      23.800     19356    0.450    3.736     100
      2      27.560       112    0.420    3.234       1
      3      32.940        69    0.420    2.717       0
      4      38.300        59    0.420    2.348       0
      5      39.400      5006    0.480    2.285      26
      6      41.260        46    0.330    2.186       0
      7      46.560      2003    0.510    1.949      10
      8      48.740        59    0.480    1.867       0
      9      56.960       236    0.510    1.615       1
     10      62.600      1156    0.540    1.483       6
     11      63.600        42    0.600    1.462       0
     12      67.040        42     ***     1.395       0
     13      71.400      1212    0.690    1.320       6
     14      76.480       683    0.750    1.245       4
     15      84.720       293    0.390    1.143       2
     16      89.640       398    0.390    1.093       2
     17      97.800       218    0.420    1.022       1
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Figure 3 The XRD pattern of the HgCdTe/Si heterojunction.

Si surface when the temperature reaches 550°C. Te may drastically react with the dangling bond on Si surface when Te reaches the Si surface [5]. According to the reference [6], $SiTe_2$ and SiTe compounds may be made at high temperature. If the produced compound is $SiTe_2$, then, the radii of $Si^{4+}$and Te^{2-} ions are 54 pm and 207 pm, respectively, the radius ratio $\frac{r_{Si^{4+}}}{r_{Te^{2-}}} = 0.261$, the value is in the range of 0.225–0.414, indicating that the two ions $Si^{4+}$and Te^{2-} are stacked in the light of tetrahedral structure with a coordination number of 4, it is known that the bonding orbital of the tetrahedral structure compound with a coordination number of 4 is SP^3 hybridization orbital [7], showing that $SiTe_2$ is bonded by means of SP^3 hybridization orbital. It can also be deduced that this compound is the cubic zincblende structure, since the diamond structure is similar to the cubic zincblende structure, which is formed by displacement of 1/4 length for the two face-centered-cubic Brarais primitive unit cells along their diagonal, noting that each set of the sublattice is composed by a kind of element, in other words, for the compound of $SiTe_2$, one set of sublattice is composed by Si, the other set of sublattice is composed by Te.

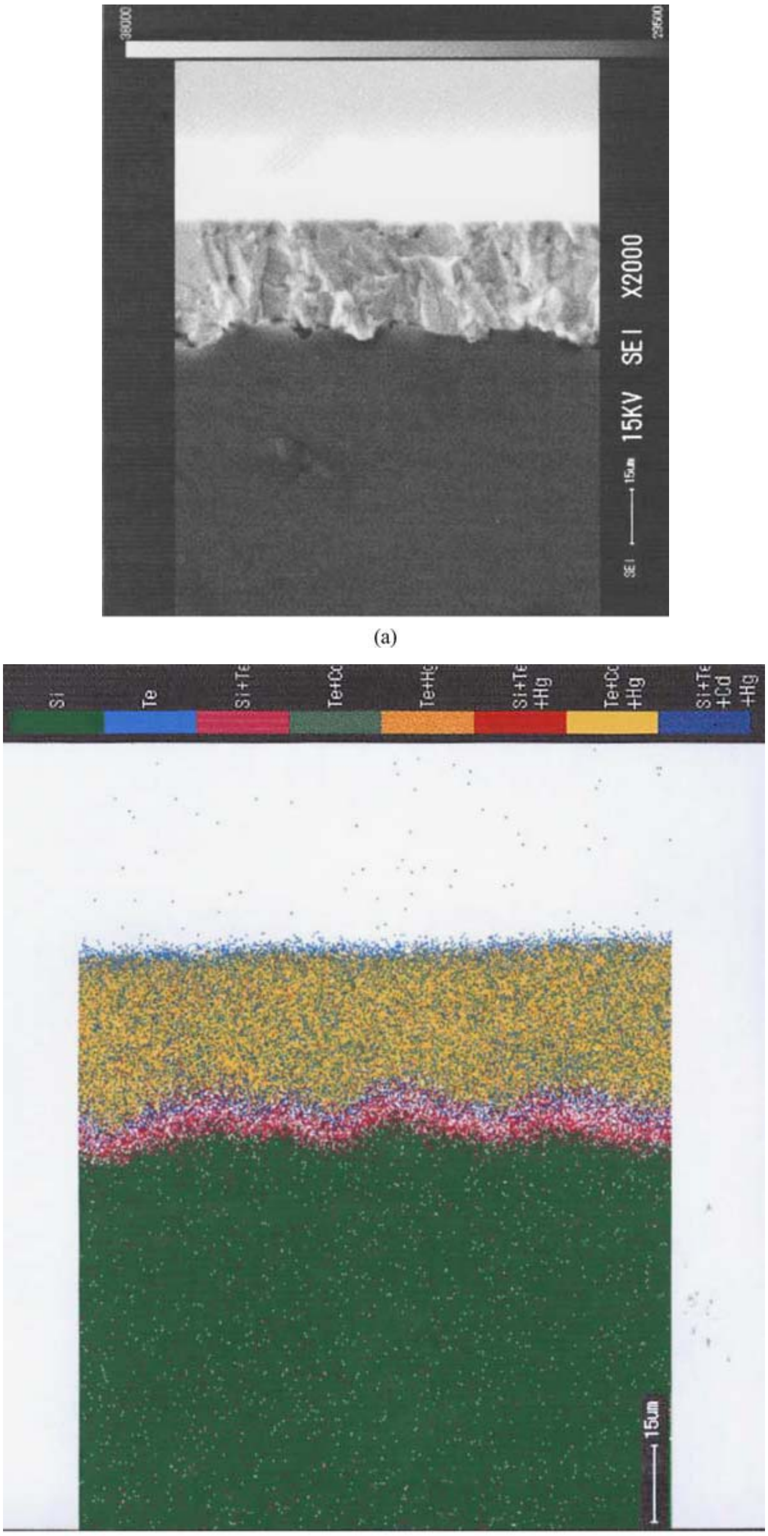
If Si reacts with Te to produce compound SiTe, then, the radii of the two ions Te^{4+} and Si^{4-} are 80 pm and 40 pm, respectively, and the radius ratio $\frac{r_{Te^{4+}}}{r_{Si^{4-}}} = 2$, the value is located in the range of ≥ 1, belonging to the most compacted pack [7]. Since Si atom is packed in the form of tetrahedral structure, it is deduced that the compound $SiTe_2$ with the same stacked structure may be the main compound on the Si substrate (the first layer of the interfacial layer), and SiTe is the minor compound on the Si substrate. But, formation of $SiTe_2$ or SiTe shows the stable chemical bond is formed between Si and Te, overcoming the drawback that big mismatch in lattice constant and thermal expansion coefficient between Si and CdTe or HgTe, providing the appetency for successive growth of CdTe or HgTe.

3.5.2. Growth of CdTe layer

It is difficulty to grow (111) oriented HgCdTe heterojunction epilayer. Its merit lies in: (a) It may consume less Hg than (100) orientation; (b) On the HgCdTe (111) B plane, the internal surface usually is plane; (c) It is easy to grow (111) oriented HgCdTe epilayer on CdTe and CdZnTe [8]. In addition, it can avoid growing circumgyrated domain from twin [5], the first growth of CdTe on the Te adsorbed Si substrate is to assure HgCdTe is grown along (111) orientation. Since CdTe is a kind of ionic compound, HgTe is a kind of semimetal, on the Si+Te layer the firstly grown CdTe is more stable due to the Cd–Te bond is more stronger than that of Hg–Te, thus, CdTe layer may be deposited by migration enhanced epitaxy.

3.5.3. Formation of Si+Te+Hg layer (the second layer in the interfacial layer)

HgTe is semimetal, the thermal conductivity is higher than that of the semiconductor CdTe. Cd and Hg belong to group II B, Hg is more active than Cd. Thus, when heating the HgTe source and adjusting the Hg vapour pressure, Hg atom may replace Cd from the grown



(a)

(b)

Figure 4 (a) the photograph of the cross section for HgCdTe/Si heterojunction (×2000) observed by EPMA. (b) the elemental distribution diagram in the cross section of HgCdTe/Si heterojunction

CdTe film, that is to say, occurring the interdiffusion that the growth rate of HgTe is much smaller than the HgTe/CdTe evaporation-interdiffusion [1]. That is why the elements in the middle layer contain Si, Te, and Hg rather than Cd, thus, the middle layer is Si+Te+Hg layer. The replaced Cd can only migrate to the third layer of the interfacial layer, therefore, the third layer is Si + Te + Cd + Hg layer.

3.6. Analysis and elemental distribution (except for Si/HgCdTe interfacial layer)

3.6.1. Analysis of the growth for epilayer at Si/HgCdTe interfacial layer

Since the third layer of the interfacial layer contains HgCdTe component, it is easy for the growth of (111) oriented HgCdTe epilayer on the interfacial layer. This is the reason that along with the increase in the size of the island composed by the same component, the column-like growth occurs in the incident vapour atom direction [9]. The area of film increases with the increase in impartial velocity of surface migration for adsorbed atoms, according with the grown morphology in Fig. 4a. As a result, (111) $Hg_{1-x}Cd_xTe$/Si heterojunction is fabricated, and the surface of the epilayer terminates with Te (shallow blue).

3.6.2. Elemental distribution in Si substrate

Fig. 4b shows that the sparse grains (Si+Te) (pink grain) homogeneously distribute in the Si substrate, this is the result of the thermal movement, which makes Si+Te component easily embeds in the Si crystal.

4. Conclusion

$Hg_{1-x}Cd_xTe$/Si heterojunction was obtained by HWE. FTIR transmission spectrum of HgCdTe was obtained, the 319.4 cm^{-1} absorption peak was measured by FTIR. This peak confirmed the existence of Si–Te bond at Si/HgCdTe interfacial layer. I-V curves indicate that a good n-HgCdTe/p-Si heterojunction may be prepared by the authors' HWE method. XRD study confirmed the formation of (111) HgCdTe on (211) Si. Morphology of a cross section observed using EPMA indicates the columnar growth of HgCdTe. An analysis of interfacial layer by EPMA indicates the presence of the three layers Si+Te, Si+Te+Hg, and Si+Te+Cd+Hg. Among them, the most important one in growth of heterojunction is the first layer. The problem of lattice mismatch and the difference in thermal expansion coefficient between Si and CdTe or HgTe may be improved by formation of Si–Te stable chemical bond through hybridization orbital bonding between Si and Te. The second and the third layers are formed by evaporation-interfiffusion process. The formation of the whole interfacial layer provides the appetency for the growth of (111) HgCdTe epilayer on Si substrate.

Acknowledgements

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