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学位論文題目	Molecular Beam Epitaxy and Characterization of β-$FeSi_2$ Thin Films （β-$FeSi_2$ 薄膜の MBE 成長と評価）
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論文内容要旨

Semiconducting silicide, iron disilicide (β-$FeSi_2$), has direct band gap of 0.85 eV at room temperature corresponding light wavelength of 1.5 μm and it also has large optical absorption coefficient (>10^5cm^{-1}, phonon energy >1 eV). β-$FeSi_2$ materials can be applied to fabricating a light-emitter working at wavelength of 1.5 μm and a light-detector at wavelength from 1.31 to 1.5 μm, which is available for the optical communication with silica-based fibers. For this reason, β-$FeSi_2$ attracts great attention for realizing its application, which focuses on epitaxial growth on silicon substrate to fabricate high performance infrared emitter and detector, as well as high efficiency solar cells. Furthermore, it is researched as thermo-generator due to its large *Seebeck* coefficient. In addition, unlike III-V or other compounds used as current optical materials, some of which are toxic, β-$FeSi_2$ is nontoxic and environmental friendly. In brief, β-$FeSi_2$ is a promising material for next generation optoelectronic and thermoelectric devices.

During the past decade, intensive investigations and efforts have been made to realize the application of β-$FeSi_2$. However, in contrast to excellent theoretical properties of β-$FeSi_2$, no practical result has been achieved in experiments. Some researchers remarked that the homogeneity and crystallinity of β-$FeSi_2$ fabricated by current methods hampered the development of practical applications. After surveying the reported β-$FeSi_2$ film growth methods, it is known that some problems are still remaining, such as the limited thickness, low purity and poor morphology, which impede the growth of high quality β-$FeSi_2$ epitaxial films, and they are difficult to be overcome by most of the reported methods. Moreover, almost all the reported methods require a high temperature annealing to complete the chemical reaction or to improve the film quality. Consequently, the degradation of the film morphology is unavoidable due to the formation of pore structure and associated islanding effect.

Unfortunately, MBE method, which is recognized as the best method for the growth of high quality β-$FeSi_2$ epitaxial film, has never been put into practice. This insufficient status calls for research and excites the present work. Thus, the present research and dissertation aim at growing high quality β-$FeSi_2$ epitaxial film directly on silicon surface by MBE method without using template technique and post-growth annealing, as described in chapter 1 of this dissertation. Other works are complementary to this core objective. It is highlighted that source materials, Fe (5N8+) has the highest purity level currently, which is applied to a practical growth for the first time. Because of employing the highest purity Fe source, β-$FeSi_2$ epitaxial film showing good structural, optical and electrical performance is expected.

Since MBE growth of β-$FeSi_2$ epitaxial film has never been reported, prior to experiments, in chapter 2 of this dissertation, the published cleaning methods for Si substrate are evaluated, and hydrogen terminated Si (111) is chosen as the suitable substrate surface for MBE growth in this dissertation. Besides, chapter 2 of the present dissertation presents many analytical methods which were performed to characterize the grown films and show definite information, such as (a) morphology: scanning electron microscope (SEM) and atomic force microscopy (AFM); (b) crystallographic information: X-ray diffraction (XRD) and transmission electron microscopy (TEM); (c) crystal composition: secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) and (e) electrical and optical characterizations: Hall effect measurement and reflective spectrum measurement. In addition, real-time reflective high energy electron diffraction (RHEED) is observed in-situ to monitor the morphology and phase of the substrate and MBE grown layers.

Hence, experiments in this dissertation proceed in the following sequence:

Chapter 3. Realizing MBE growth of β-$FeSi_2$ epitaxial film (investigating the optimal growth condition);
Chapter 4. Clarifying the MBE growth mechanism;
Chapter 5. Improving the quality of MBE grown β-$FeSi_2$ epitaxial film;
Chapter 6. Characterizing MBE grown β-$FeSi_2$ epitaxial films (Electrical and optical characterizations).

Chapter 3: In order to realize MBE growth of β-$FeSi_2$ epitaxial film and to investigate the optimal growth condition, the experiments concerning the research on effects of substrate temperature and Fe/Si flux ratio are individually carried out, as marked in two dot-lines in Fig. 1. As for experiments on the effects of substrate temperature, samples are grown with stoichiometric Fe/Si ratio of 0.5 at various substrate temperatures (T_s) from 480 °C to 660 °C by an increase of about 20-50 °C. By analyzing XRD, it is found that the growth at lower T_s presents films containing ε-FeSi, while the growth at higher temperature gives a polycrystalline β-$FeSi_2$ film. By observing SEM, it is verified that the epitaxial films grown at 580 °C shows better surface morphology than other samples grown at higher T_s. Thus, the optimal growth temperature is concluded at 580 °C.

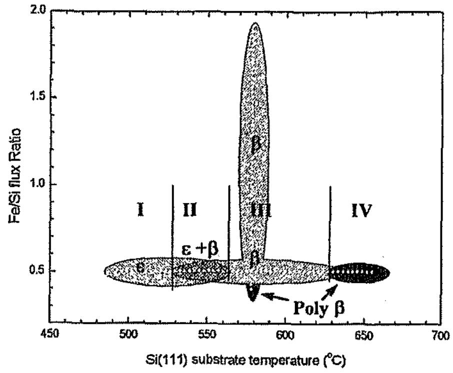

Fig. 1 Film phase composition as a function of Fe/Si source flux ratio and substrate temperature.

For the purpose of studying the effect of Fe/Si flux ratio, another series of films are grown at the optimal substrate temperature (T_s=580 °C) with varying Fe/Si ratio from 2 to 0.4 as shown in Fig. 1. XRD results verify that all films grown at 580 °C is single β-$FeSi_2$ phase. It is detected by SEM that the grown film morphology will be improved along the decreased Fe/Si ratio. However, the growth with a flux ratio smaller than stoichiometric Fe/Si ratio (0.5) presents a polycrystalline film. Therefore, it is concluded that the optimal growth condition, for the present MBE growth of β-$FeSi_2$ on hydrogen terminated Si (111) substrate, is T_s=580 °C and Fe/Si=0.5.

Films grown under the optimal growth condition are further characterized by observing RHEED and TEM. The characterization results confirm the epitaxial growth of β-$FeSi_2$ films on Si (111) substrate.

Chapter 4: A clear understanding of the involved mechanisms is a prerequisite for the growth of high quality film, however, the growth process of β-$FeSi_2$ epitaxial film by MBE, that is to say, how the Fe and Si crystallize on Si surface and subsequently form a thick β-$FeSi_2$ epitaxial layer has never been reported and continually observed. Therefore, after realizing MBE growth of β-$FeSi_2$ epitaxial film, the MBE growth mechanism is further investigated.

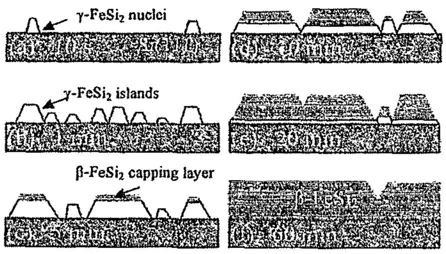

Fig. 2 *Sketches for the film structure and phase* development, depending on the growth time.

A series of samples are grown under the established optimal growth condition with different growth times ranging from 10 seconds to 1 hour. RHEED, XRD and AFM analyses are conducted to monitor and to examine the morphology evolution and phase development.

By analyzing the characterization results, a model for MBE growth mechanism is proposed and sketched out, as shown in Fig. 2. It is revealed that, during MBE growth of β-$FeSi_2$, γ-$FeSi_2$ phase grows first in 3-D mode, as illustrated in Fig. 2(a) and (b). After reaching the critical thickness, there undergoes a strain-induced transition towards β-$FeSi_2$ phase on the surface of 3-D γ-$FeSi_2$ islands, as shown in Fig. 2(c). In the following stages, on β-$FeSi_2$ layer, the Fe and Si atoms epitaxially grow in 2-D mode, whereas on γ-$FeSi_2$ islands they grow in 3-D mode until the phase transition towards β-$FeSi_2$ happens, corresponding to Fig. 2(c)-(d). After that, the islands capped β-$FeSi_2$ layer expand in lateral, merge each other and finally cover the entire surface area, as shown in Fig. 2(e). Simultaneously, the buried γ-$FeSi_2$ phase layer gradually transforms to β-$FeSi_2$ phase driven by thermal heating. Consequently, it forms a crystal film in single β phase, as drawn in Fig. 2(f).

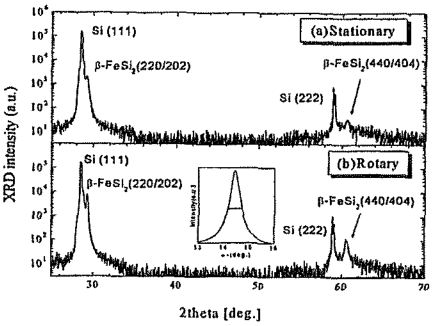

Fig. 3 XRD spectra of the films grown on (a) stationary and (b) rotary Si (111) substrate .

Chapter 5: It is reported by many researchers that, during MBE growth, rotating the substrate is an effective technique that can diminish the source geometric effect and achieve a uniform growth, and thereby improve the grown film homogeneity, as well as increase the film thickness. However, rotation technique is sacrifice for RHEED observation in previous experiments. In the present experiments, substrate rotation will be applied to MBE growth of β-$FeSi_2$ epitaxial film.

In order to research the relevant effects, two kinds of samples are grown on a stationary or rotary Si (111) substrate under the established optimal growth condition and the rotation effects are evaluated from the viewpoints of morphology, crystallinity, film thickness and purity by using SEM, XRD, SIMS and GDMS, respectively.

Fig. 3 presents the XRD patterns observed from two samples grown on stationary or rotary substrate. Since only diffraction peaks related to Si (111) and β-$FeSi_2$ (110/101) exist in both samples, it proves that both films are epitaxially grown on Si (111). However, β-$FeSi_2$ peaks intensities *of the sample grown on a rotary Si (111)* are several times stronger than those of the sample grown on the stationary Si (111), while Si peaks intensities are almost same for both samples. It indicates that the rotation can improve the β-$FeSi_2$ epilayer thickness and crystallinity. The insert shown in Fig. 3(b) is the rocking curve of β (220/202) peak for β-$FeSi_2$ film grown on a rotary Si (111) substrate. The full width at half maximum (FWHM) value is 0.55°. It proves that MBE grown β-$FeSi_2$ epitaxial film shows better crystallinity than the reported β-$FeSi_2$ films grown by other methods, which have an average FWHM of about 1.0°.

SIMS profile agrees with the XRD results and reveals that rotation significantly increases the thickness of the grown β-$FeSi_2$ film from 80 nm to 160 nm. Analyzing SEM images shows that MBE growth with rotation achieves a uniform morphological surface. By analyzing SIMS and GDMS data, it is found that substrate rotation introduces the nonmetallic impurities, but it does not further affect the concentration of metallic impurities. It is confirmed that for MBE growth of β-$FeSi_2$ film, substrate rotation is essential for growing large-size epitaxial films having better morphology, crystallinity and purity than all reported β-$FeSi_2$ films grown by other methods.

Chapter 6: After realizing the growth of high quality β-$FeSi_2$ epitaxial film, the research in this dissertation proceeds to electrical and optical characterizations.

Hall effect measurement is analyzed to investigate the carrier transport properties. It is found that a moderate thermal annealing can improve and regularize the hole mobility of β-$FeSi_2$ film. Fig. 4 is the measured temperature-dependent (T-dependent) hole mobility for β-$FeSi_2$ film annealed under appropriate annealing regime, which is defined at 780 °C for 10 hours. The fitted slope for T-dependent mobility from 100 K to room temperature shows n=3.7. It agrees with the previous report that only β-$FeSi_2$ grown from high purity starting materials can present n value larger than 3. In addition, a maximum hole mobility, 21,000 cm^2/vs is obtained at 45 K, which considerably exceeds those of all reported films grown by other methods.

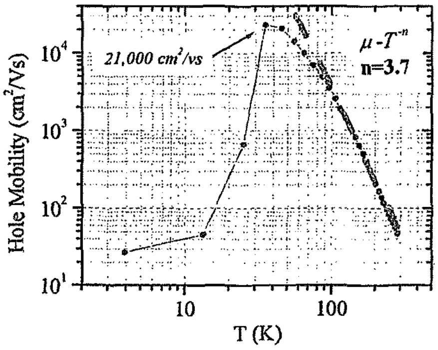

Fig. 4 Hole mobility for annealed β-$FeSi_2$ epitaxial film. Dash line showing T-dependent mobility relation.

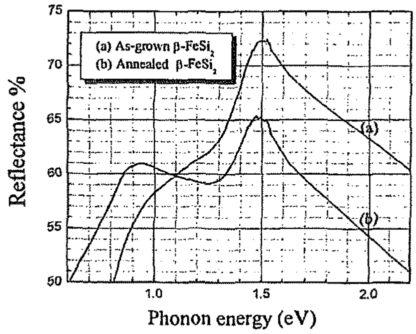

Fig. 5 Reflective spectra of MBE grown β-$FeSi_2$ films (a) as-grown and (b) annealed at 780 °C for 10 h.

To study the annealing effect on crystallinity, reflective spectrum is measured. Fig. 5 reveals that, after annealing, multi reflectance maximum appear, which indicates higher structural perfection. To confirm the improvement of crystal quality, rocking curve of curve of β (220/202) is measured as shown in Fig. 6, and FWHM value is further decreased to 0.07° for annealed β-$FeSi_2$ film. This is the best value up to now, and almost by one order smaller than the reported results on β-$FeSi_2$ films. It gives direct evidence that MBE is superior to all other methods.

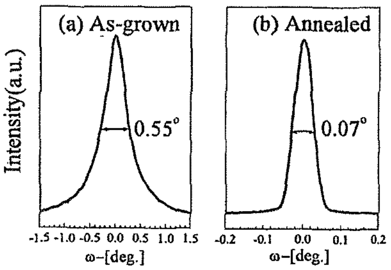

Fig. 6 Rocking curve of β-$FeSi_2$ (220/202) (a) as-grown and (b) annealed at 780 °C for 10 h.

In chapter 7 of this dissertation, it is summarized that, for the first time, a direct growth of β-$FeSi_2$ epitaxial film on Si (111) is successfully achieved by using MBE without template layer and post-growth annealing, and the relevant MBE growth mechanisms are clarified. The structural, electrical and optical characterizations results strongly agree with each other and demonstrate that, using the highest purity material Fe (5N8+), MBE method realizes the growth of high purity, high quality β-$FeSi_2$ epitaxial film better than all reported β-$FeSi_2$ epitaxial films grown by other methods, which perfectly accords with the expectation of this dissertation.

論文審査結果の要旨

β-$FeSi_2$は禁制帯幅0.85eVを有する直接遷移型化合物半導体であり、耐環境性に優れた次世代の赤外域受発光素子用材料として注目されている。しかしながら、デバイス作製に必要なエピタキシャル膜の成長は実現されていない。本論文は、超高純度FeおよびSiをソースとして用い、水素終端処理を施したSi(111)基板上に、分子線エピタキシー法により初めてβ-$FeSi_2$エピタキシャル膜の直接成長に成功した経緯を纏めたものであり、全７章より構成されている。

第１章は緒論であり、本研究の背景と目的について述べている。

第２章は実験方法であり、本研究で用いた分子線エピタキシー装置および評価手法について述べている。また、Si基板の処理方法について実際に実験を行い、水素終端処理が最も適した方法であることを明らかにしている。

第３章では、RHEED、XRDおよびTEM観察により、成長条件の最適化を行っている。Fe/Si供給比を0.5に固定し、基板温度の影響を調べた結果、基板温度580℃において、β-$FeSi_2$エピタキシャル膜の成長が始めて確認された。また、基板温度が低い場合にはε相が出現し、逆に高い場合にはβ-$FeSi_2$多結晶膜が得られた。さらに、成長温度を580℃に固定し、Fe/Si供給比を変化させ、Fe/Si供給比0.5が最適であることを明らかにしている。

第４章では、エピタキシャル成長の機構を明らかにしている。RHEEDによる直接観察、XRDおよびAFM観察の結果を総合し、まず、準安定であるγ相が基板上に３次元成長し、臨界厚さに到達後応力緩和によりβ相がγ相先端に成長する。その後、β相が２次元成長するというモデルを提案している。さらに、界面のγ相は成長温度でβ相に変態することを実験的に明らかにし、モデルの妥当性を検証した。

第５章では、成長膜の組成、純度および表面形態に及ぼす基板回転の影響を調べている。静止基板上に成長したβ-$FeSi_2$エピタキシャル膜において、表面にクレータ状の窪みが認められたが、基板回転により平坦な表面モフォロジーが得られることを示した。

第６章では、成長結晶の結晶性、電気的特性に与えるアニールの影響を調べている。780℃で１時間アニール後、ドメイン構造の成長が認められ、X線ロッキングカーブの半値幅は、0.55度とこれまでの報告値の1/10であった。また、成長結晶はp型で、ホール移動度は21000cm²/Vsとこれまでの報告値を上回る値が得られ、成長結晶が高品位であることを明らかにした。

第７章は結論で、本研究で得られた成果を総括している。

以上要するに、本研究は、これまで困難であったβ-$FeSi_2$/Siエピタキシャル膜の直接成長に初めて成功したもので、材料工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。