DEVELOPMENT OF MATERIAL ANALYSIS FACILITY IN KU-FEL*

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Abstract

A mid infrared free electron laser (MIR-FEL) (5-20 µm) facility (KU-FEL: Kyoto University Free Electron Laser) has been constructed for contributing to researches on energy science at Institute of Advanced Energy (IAE), Kyoto University. The first laser power saturation at 13.2 µm was achieved in May 2008. After laser saturation, we had constructed a new facility of MIR-FEL application for developing energy science in KU-FEL, and we started two researches of MIR-FEL application. One of the researches is selective phonon excitation by MIR-FEL for investigation of the relation between lattice vibration (phonon) and electronic structure. And another research is two-color, two-photon excitation by MIR-FEL and Nd-YAG laser for precise measurement of the energy band. The two researches of MIR-FEL application are in progress.

INTRODUCTION

The MIR region light such as MIR-FEL corresponds to the absorption wavelength of molecular and lattice vibration. Therefore, by irradiating MIR-FEL to material, we can excite a specific chemical bond in the material, or we can break a specific chemical bond selectively [1]. After achieving laser saturation, application facility of KU-FEL (material analysis facility) was planned to contribute to the research of renewable energy such as photosynthesis, photocatalyst and organic thin film solar cells. And six measurement systems, which are photoluminescence (PL) spectrometer, photoelectron spectrometer in air, high speed atomic force microscope, high performance liquid chromatography mass spectrometry, super centrifuge and ICP atomic emission spectrometer, were installed in material analysis facility. After installation of measurement systems, FEL transport line was connected to PL spectrometer. The connection between FEL transport line and the other measurement systems is under construction. By using the PL spectrometer with MIR-FEL, we started the researches of MIR-FEL application. One of researches is selective lattice vibration (phonon) excitation by MIR-FEL for the clarification of the relation between phonon and electronic structure. Another research is two-color, two-photon excitation by MIR-FEL and Nd-YAG laser for a precise measurement of energy band. In this paper, we will briefly introduce the material analysis facility, and the two researches of MIR-FEL application in PL spectrometer section.

MATERIAL ANALYSYS FACILITY

Figure 1 shows the schematic figure of material analysis facility in KU-FEL. At first, PL spectrometer had been installed in material analysis facility. After the installation of the PL spectrometer, other measurement systems, which are photoelectron spectrometer in air, high speed atomic force microscope, high performance liquid chromatography mass spectrometry, ICP atomic emission spectrometer and super centrifuge, were installed.

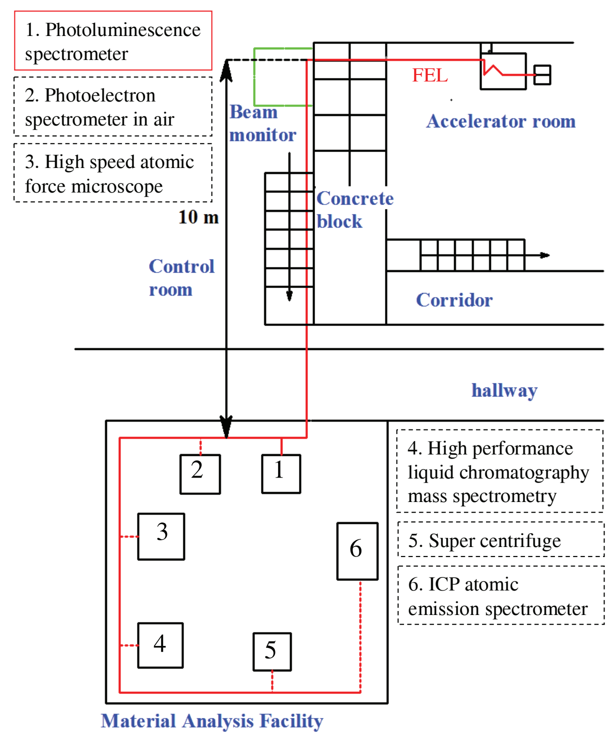

Figure 1: Schematic figure of material analysis facility in KU-FEL. No.1~6 shows the name of the installed measurement systems. Dotted boxes mean that the measurement system has not connected to MIR-FEL transport line.

The objective of PL spectrometer with MIR-FEL is the investigation of electronic structure in the material with exciting the lattice vibration. And, a photoelectron spectrometer in air can evaluate the surface condition of the solid material. In addition, we can modify the surface of material by MIR-FEL irradiation [1]. Therefore, by combining a photoelectron spectrometer in air with MIR-FEL, we can evaluate the surface condition modified by MIR-FEL, and the photoelectron spectrometer with MIR-FEL will contribute to the evaluation of thin film solar cells because researches of surface modification were done in thin film solar cells to improve the conversion efficiency.

High speed atomic force microscope can observe the surface of the solid material or liquid as movie as well as pictures [2]. Therefore, by using the high speed atomic force microscope with MIR-FEL, we can observe the transformation of proteins or DNA induced by excitation of a specific chemical bond by MIR-FEL irradiation. And the observation of the transformation will contribute to the research in the field of chemistry, and biochemistry such as photosynthesis.

High performance liquid chromatography mass spectrometry, ICP atomic emission spectrometer and super centrifuge are used for the identification of substance such as aromatic substance, fragment of protein, and metal element in the liquid. And MIR-FEL can break a specific chemical bond selectively [1]. Therefore, by combining these three systems with MIR-FEL, we can identify the substance produced by MIR-FEL irradiation in the liquid, and these three systems with MIR-FEL will contribute to the research of new chemical pass induced by MIR-FEL.

MIR-FEL is irradiated from the accelerator section, and transported by gold mirrors. The details of MIR-FEL transport line is shown in previous report [3]. Finally, the transported MIR-FEL is delivered to each measurement systems. Right now, the PL spectrometer has been connected with MIR-FEL transport line. Therefore, in the following section, we will introduce the application research by using PL spectrometer with MIR-FEL.

Selective Phonon Excitation

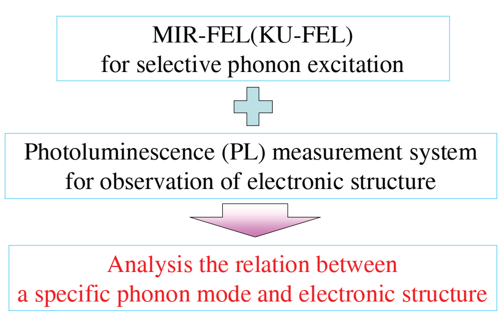

Figure 2: Composition of the system for selective phonon excitation.

Wide gap semiconductors such as TiO_2 and SiC are attracting interests as an electrode of solar cells, a next generation materials for power devices, and photocatalyst materials. These materials show unique electrical and optical properties through coupling of lattice vibration (phonon) with electronic structures [4]. However, the relation between phonon and physical properties has not been clarified. Therefore, a new method which is able to excite a particular phonon is indispensable for a deep understanding of the relation between phonon and electronic structure as well as development of wide gap semiconductor devices.

In Fig. 2, the composition of the system for selective phonon excitation is shown. It is well known that MIR region light resonates with phonon in solid materials such as SiC. Owing to the features of FEL such as high power and short pulse, it is considered that the radiation of MIR-FEL gives rise to the change in physical and electronic properties by exciting a specific phonon mode. In addition, the PL spectrometer is used for the analysis of electronic structure of solid. Therefore, by combination with MIR-FEL and PL spectrometer, the relationship between a particular phonon and electronic structure of a solid material can be investigated.

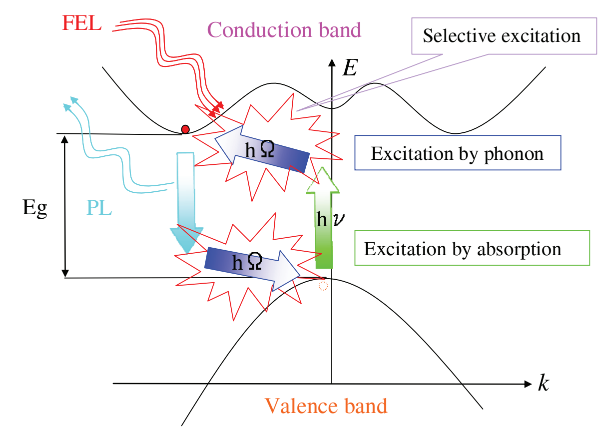

Figure 3: Considerable interaction model of electron transition induced by MIR-FEL irradiation in indirect semiconductor

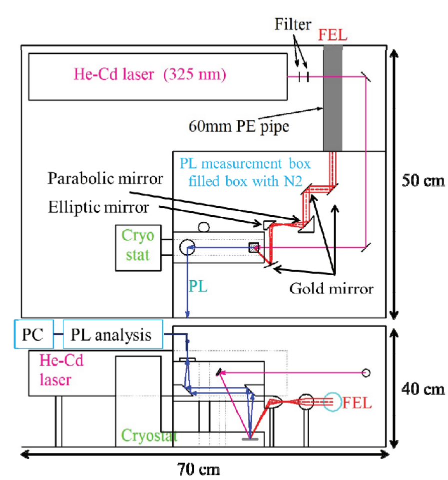

Figure 4: Design of the system for selective phonon excitation.

And, as a pilot sample to verify the principle that MIR-FEL irradiation excites a specific phonon selectively, silicon carbide (SiC) was selected. Because SiC has an absorption wavelength of lattice vibration in 12.5 µm, and this wavelength corresponds to the tunable wavelength of KU-FEL [5]. In addition, SiC is indirect type semiconductor. When the electron transition happens in indirect semiconductor, the kinetic energy (K) and photon energy (E) are needed. Therefore, when the selective

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excitation of lattice vibration initiated by a radiation of MIR-FEL tuned in absorbance wavelength of lattice vibration of SiC, the kinetic energy will be supplied to electron. And the change of PL spectrum will be observed. In Fig. 3, the considerable interaction by irradiating MIR-FEL to SiC is shown.

In Fig. 4, the design of the system for selective phonon excitation is shown. The PL system consists of He-Cd laser, a monochromator and a CCD detector. A monochromator and a CCD detector are installed in PL analysis section. Data from the CCD detector are collected in PC. To evaluate the temperature dependence of the PL spectrum, temperature down to 10 K is achieved by using a closed cycle He refrigerator. For synchronous irradiation of MIR-FEL and He-Cd laser, the accelerator trigger is used in both MIR-FEL and CCD detector for the trigger of PL measurement system. The transported FEL beam is focused by using a parabolic mirror and an elliptic mirror. By installing a beam splitter between the parabolic mirror and the elliptic mirror, the property of irradiated FEL beam is monitored during measurement. And the PL measurement box for covering the optics is filled with N_2 gas to prevent the absorption of MIR-FEL by air.

Two-color, Two-Photon Excitation

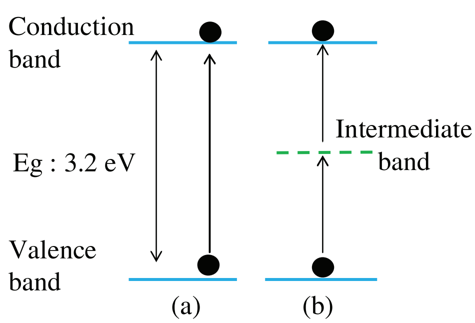

Figure 5: Electron transition model of TiO2 (a) Before surface modification, (b) After surface modification.

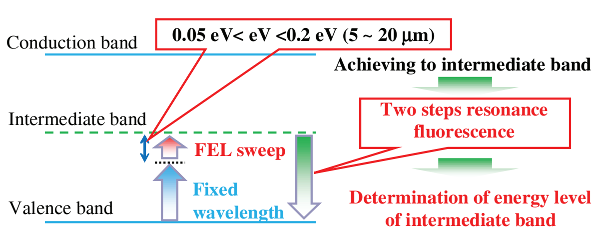

Figure 6: The schematic figure of the measurement principle.

Photocatalyst such as TiO_2 is investigated to enhance the photocatlytic activity under visible-light illumination [6]. Because photocatalytic activity of TiO_2 is available only under ultraviolet (UV) light at the wavelength of shorter than 400 nm which is a small fraction (about3 – 4%) of total solar spectra on the earth. Therefore, many researchers are investigating how to enhance the photocatalytic activity under visible-light illumination. One of the solutions to enhance the photocatalytic activity is the surface modification. By the surface modification of TiO_2, it is considered that intermediate band is produced between conduction band and valance band[6]. By the intermediate band, the photon energy required for exciting electrons from valance band to conduction band is reduced. Therefore, the photocatalytic activity under visible-light illumination is enhanced. In Fig. 5, the electron transition model of TiO_2 is shown.

Technique such as surface modification is also used for the improvement of thin film solar cells [7]. Therefore, to develop the functional material such as photocatalyst and thin film solar cells, the understanding about the energy level of intermediate band is indispensable.

In our group, we proposed a method to measure energy level precisely by using MIR-FEL. In Fig. 6, the schematic figure of the measurement principle is shown. Two lasers is used in the method, which are MIR-FEL and fixed wavelength laser. Two lasers is irradiated simultaneously, the wavelength of MIR-FEL is swept. And, when the sum of the energy of both MIR-FEL and fixed wavelength laser reaches the energy level of intermediate band, PL will be observed. Therefore, by measuring the wavelength dependence of PL intensity, we can measure the energy level of intermediate band precisely.

Two-color, two-photon excitation by MIR-FEL and fixed wavelength laser has several advantages. The biggest advantage is that this method can measure energy level precisely. Because the energy of fixed wavelength laser is determined in theory, and we can change the wavelength of MIR-FEL exactly by changing undulater parameter and electron energy, in addition, the energy resolution of MIR-FEL is higher than other tunable laser such as dye laser. And next advantage is that the high S/N ration is promising in the spectrum because the MIR-FEL is high power laser. The third advantage is that we can change the measurement wavelength region by changing the combination of lasers. For example, by using dye laser and MIR-FEL, the measurement wavelength region will be more widely

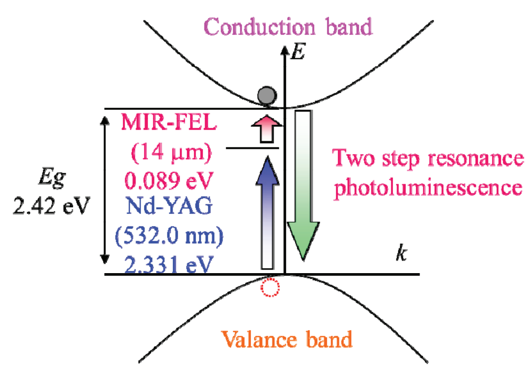

Figure 7: The schematic model of the verification of the principle.

Luminescence by two-color, two-photon excitation was reported previously [8]. In the report, a dye laser as probe

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laser and an Nd-YAG laser as pump laser were used. However, it is not proved that the MIR-FEL and Nd-YAG laser can be used as the laser for two-color, two-photon excitation. Therefore, at first, we have to verify the principle that two step resonance photoluminescence is radiated by MIR-FEL and fixed wavelength laser.

For the verification of the principle, cadmium sulfite (CdS) was selected as standard material, and Nd-YAG laser is selected as fixed wavelength laser. Second harmonic generation of Nd-YAG laser will be used. Because the band gap energy of CdS is 2.42 eV, and this value matched the sum of the energy of both MIR-FEL (14 μm: 0.089 eV) and Nd-YAG laser (532.0 nm: 2.331 eV) [9]. And the CdS has no absorbance of lattice vibration mode in 12~14 μm. Therefore, the selective phonon excitation is not happened by MIR-FEL. In Fig. 7, the schematic model of the verification of the principle is shown.

Now this experiment is progressive and we will report about result later.

CONCLUSION

Material analysis facility, which is application stations of MIR-FEL were constructed in KU-FEL. Measurement systems, which are PL spectrometer, photoelectron spectrometer in air, high speed atomic force microscope, high performance liquid chromatography mass spectrometry, super centrifuge and ICP atomic emission spectrometer, were installed. And the FEL transport line was connected to PL spectrometer. Researches of MIR-FEL application by using PL spectrometer started. One of the researches is verification of selective phonon excitation by MIR-FEL for deep understanding of the relation between phonon and electronic structure. And another research of MIR-FEL is two-color, two-photon excitation by MIR-FEL and Nd-YAG laser for precise measurement of energy level. These researches are in progress.

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