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Material Analysis Laboratory in KU-FEL, Kyoto University

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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. Up to now 12~14 μm FEL has been generated. The MIR-FEL, which is tunable and high peak power with a short pulse, could excite the molecular bond and the lattice vibration mode selectively or break a specific chemical bond. This is due to that wavelength of MIR-FEL match vibration modes of materials. The unique properties of MIR-FEL such as selective excitation of vibration mode can apply in biochemistry, chemistry, and solid physics. Therefore, in our facility, MIR-FEL is applied for the evaluation system, production of solar cell, research of photocatalyst and so on. For the research of energy science with using MIR-FEL, Material Analysis Laboratory (MAL) has constructed. The KU-FEL facility with the MAL is open to world-wide users.

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Keywords: MIR-FEL; material Science ; material evaluation

1. Introduction

Mid infrared free electron laser (MIR-FEL) facility at Institute of Advanced Energy (IAE), Kyoto University has been constructed and the first laser power saturation at 13.2 μm was observed in May 2008 [1]. FEL has attractive features such as tunable wavelength, short pulse, and high power. MIR-FEL has

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been applied to photolysis of Freon [2], annealing of diamond [3], novel thin film fabrication [4], selective removal of cholesterol ester [5], modification of tooth [6], analysis of molecular structure [7] and so on.

In the IAE, the research of energy science has been pursued to help in the reduction of carbon emission. For example, improvement of performance of solar cell, biomass fuel production, and photocatalyst have been studied. To boost these researches, an application station of MIR-FEL called as Material Analysis Laboratory (MAL) has been constructed. Because MIR-FEL tuned in the absorption wavelength of chemical bond can excite or break a specific chemical bond selectively [8]. The selective excitation can be employed for modification of surface of substance and a photoreaction path of catalyst surface over conventional photoreaction [9]. In MAL, we have planed to install the following six evaluation systems..

At first, photoluminescence spectrometer has been installed to conduct a research for the relation between lattice vibration (phonon) and electronic structure. Next, a photoelectron spectrometer in air has been installed for the evaluation of surface of electrode of thin film solar cell such as dye sensitized solar cell. Super centrifuge, high performance liquid chromatography mass spectrometer, and ICP atomic emission spectrometer have been installed for the detection and separation of substance produced by new photochemical path introduced by MIR-FEL radiation. Finally, high speed atomic force spectrometer has been installed for research of behavior of enzyme. In this paper, we briefly describe these evaluation systems installed in MAL. Typical applicable research for each evaluation system is introduced as well.

2. Kyoto University Free Electron Laser

FEL is this kind of laser which uses a high energy electron beam as a laser media. In Fig.1, the FEL principle is shown, and can be described as; at first, electron beam, which is accelerated close to the light velocity, is injected into the undulator and wiggled by the undulator field. Undulator is a device to irradiate synchrotron radiation by periodically altered magnetic field. The synchrotron radiation is stored in an optical resonator. This one interacts with electron beam, and then the optical power is enhanced up to around 10^6 times of initial power. Finally, stored radiation becomes coherent light. In Table 1, the FEL properties of KU-FEL are shown. FEL has a specific pulse structure consisted of micro pulse and macro pulse, the former width in KU-FEL is less than 1 ps and peak power is around 2 MW. Macro pulse consists of ~ 3000 micro pulses during 1 μs pulse duration, with power of 5 mJ. Wavelengths 12 ~ 14 μm is the tunable range of FEL which can be changed by changing energy of electron beam and intensity of undulator field. Therefore, FEL can be used as high power pulse laser with continuously tunable

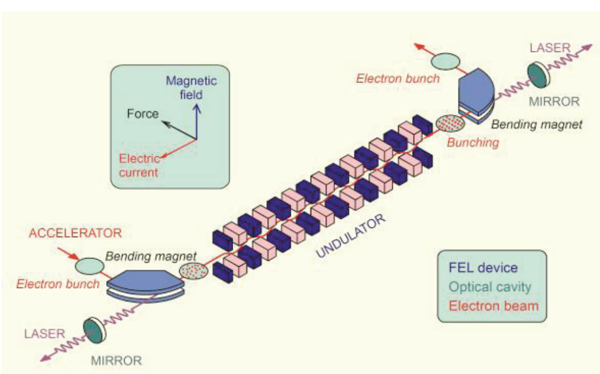

Fig. 1. Principle of FEL.

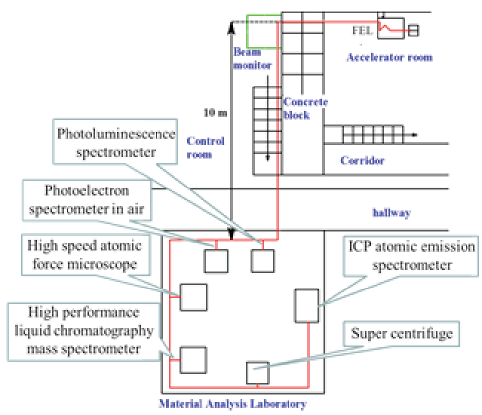

Fig. 2. Schematic figure of MAL.

Table 1. FEL properties of KU-FEL [1].

FEL properties (13.2 μm)		
	Micro pulse	Macro pulse
Pulse width	<<1 ps	1 μs
Pulse energy	2 μJ	5 mJ
Power	2 MW	5 kW
Tunable wavelength	12 μm ~ 14 μm	

wavelength.

Material Analysis Laboratory

MAL has been constructed in the KU-FEL facility for contributing to the development of energy science. In Fig.2, the schematic drawing of MAL is shown. The MIR-FEL is generated in the accelerator room and transported by gold mirrors which can reflect 5 ~ 20 μm light less than 5 % losses. MIR-FEL beam was transported by poly ethylene (PE) beam pipe which is filled with N_2 gas to prevent the absorption by water vapor and CO_2 [1]. Then transported FEL beam is delivered to the evaluation systems, a photoluminescence spectrometer, a photoelectron spectrometer, a high speed atomic force microscope, a high performance liquid chromatography mass spectrometer, a super centrifuge, and an ICP atomic emission spectrometer, installed in MAL. In the following subsections, we will introduce these six evaluation systems and the applicable applications of MIR-FEL.

2.1. Photoluminescence spectroscopy

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 [10]. 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 for development of wide gap semiconductor devices.

It is well known that MIR region light resonates with phonon in solid materials such as SiC [11, 12]. 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 photoluminescence (PL) spectrometer is used for the analysis of electronic structure of solid. Therefore, by combination with MIR-FEL and photoluminescence spectrometer, the relationship between a particular phonon and electronic structure of a solid material can be investigated.

In Fig.3, the schematic drawing of PL system combined with MIR-FEL is shown. The PL system consists of He-Cd laser (wavelength: 325 nm, power: 10 mW, beam diameter: 1.0 mm: Kimmon IK5451R-E) and a monochromator (Zolix Omni-λ, 300) and a CCD detector (INTEVAC Mosir 350). 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 for the trigger of PL measurement system. In the PL analysis section, a CCD (Charge Coupled Device) detector is used to receive the material response. Data from the CCD detector are collected in PC [1]. The optics of the PL system is shown in Fig.4. 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.

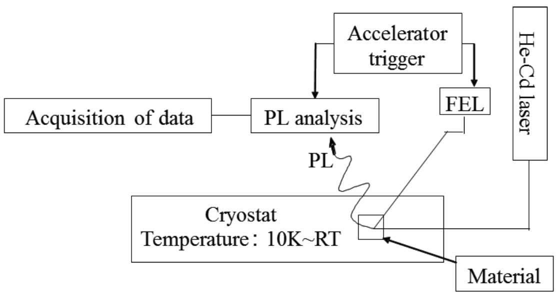

Fig. 3. Schematic drawing of PL system.

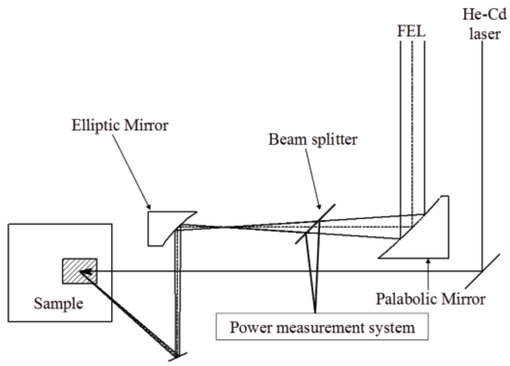

Fig. 4. Optics of PL system.

As the first experiment, SiC is used as a material to verify the principle that MIR-FEL can excite the phonon selectively. The wavelength of lattice vibration of SiC corresponds to the KU-FEL tunable range and SiC is indirect type semiconductor, therefore SiC is suitable material for the verification of selective phonon excitation. Figure 5 shows a schematic drawing of electron excitation of an indirect type semiconductor and indicates the excitation of the electrons by the effect of phonon. Therefore, when the selective excitation of lattice vibration initiated by an 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. Therefore, the change of PL spectrum proves that MIR-FEL affects to phonon and precise information on the electronic structure will be extracted.

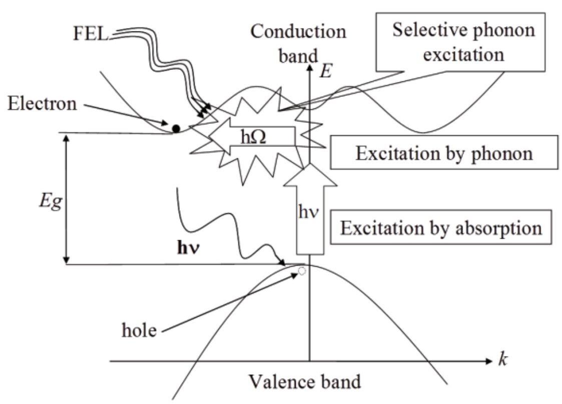

Fig. 5. Schematic model of electron excitation of indirect semiconductors

2.2. Photoelectron spectroscopy in air

Solar cells made by silicon are widely used in the world. On the other hand, thin film solar cells such as dye sensitized solar cells and organic solar cells are attractive as the next generation solar cells, because the production cost is cheaper than that of silicon. However, the conversion efficiency of the next generation solar cell is less than 10 % [13]. Therefore, the method to increase the conversion efficiency of next generation thin film solar cell is critical. One possible methodology is the surface modification [14, 15]. MIR-FEL can be applied for the surface modification of the organics on the surface of electrode. Since MIR-FEL can break the specific chemical bond selectively, we can control the substitute of chemical substance on surface.

Photoelectron spectrometer is used for the evaluation of surface condition of materials by measuring ionization energy, because the ionization energy depends on the surface condition of the materials. The photoelectron yield spectrometer (RIKEN KEIKI Co., Ltd. MODEL AC-3) installed in MAL operates at atmosphere pressure. Therefore, the photoelectron yield spectroscopy is applicable for any form of sample, such as liquid and powder for the thin film solar cell.

The procedure of surface evaluation system by MIR-FEL is shown in Fig.6. The main target of the photoelectron yield spectrometer is evaluation of surface condition of dye sensitized solar cell and organic thin film solar cells. We will modify the surface of these next generation solar cells by using MIR-FEL, and the optimum surface condition of thin film solar cells are studied.

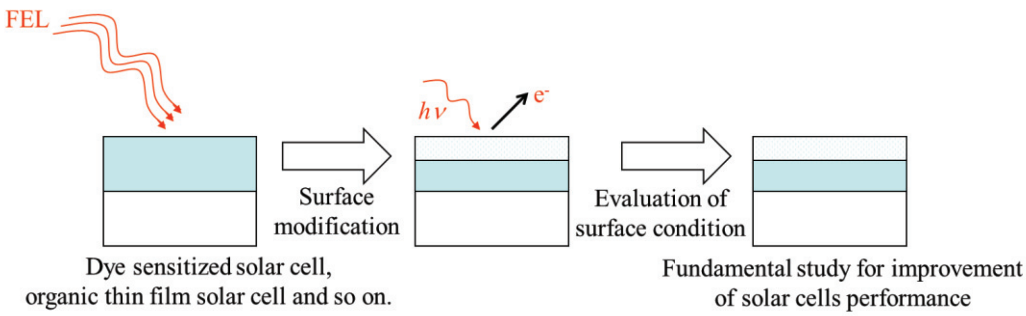

Fig. 6. Procedure of MIR-FEL evaluation system of surface.

2.3. Super centrifuge, high performance liquid chromatography mass spectrometry, ICP atomic emission spectrometer

Photocatalyst, such as TiO_2, is a famous material which converts H_2O to H_2 and O_2 [16]. In addition, photocatalyst is known as the material which decomposing the harmful substances, such as dioxin [17]. It is reported that MIR-FEL radiation to the surface of catalyst such as MoO_3 introduced a new photochemical path by resonance between wavelength of lattice vibration of catalyst and wavelength of MIR-FEL [9]. The research of new photochemical path introduced by MIR-FEL irradiation will contribute to the development of new catalytic process by excitation of a specific lattice vibration.

To analyze the path of specific chemical reaction, the detection or separation of reaction products is needed. Three systems, super centrifuge (optima MAX-XP, Beckman Coulter), high performance liquid chromatography mass spectrometer (AccuTOF LC-plus (JMS-T100LP), JEOL), and ICP emission spectrometer (Thermo Fisher Scientific, iCAP6300 Duo) are installed in MAL. High performance liquid chromatography mass spectrometry is used for the detection of small organic substance such as aromatic compounds. The super centrifuge is used for the separation of big organic substance such as the proteins and DNA in liquid. The ICP atomic emission spectrometer is used for the identification of elements such as metals in liquid, the experimental procedure with MIR-FEL is shown in Fig. 7. Therefore, by using these three systems, many kinds of substance produced by a new photochemical path can be separated or identified with high accuracy.

In addition, high performance liquid chromatography mass spectrometer and super centrifuge assisted by MIR-FEL can apply for the biochemical research such as the research of modification of protein, because we can break the specific chemical bond in the proteins [7]. These three systems promote the photochemical research such as photocatalyst, photolysis, and photosynthesis.

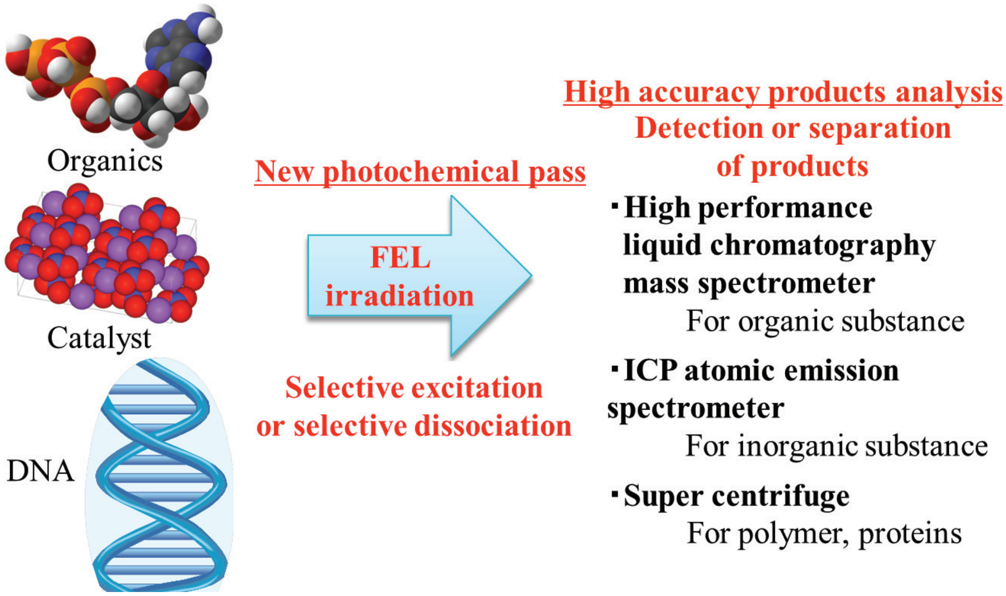

Fig. 7. Procedure of three systems with MIR-FEL.

2.4. High speed atomic force microscope

Biomass fuel such as bioethanol is investigated as an alternative fuel of the fossil fuel. The main production process of the biomass fuel is fermentation by enzyme. In the production process of biomass fuel by enzyme, enzyme has optimum temperature for fermentation. For example, optimum temperature of amylase is around 30 ºC. The reason why the enzyme has optimum temperature is the enzyme reaction depends on the conformation of the enzyme. Therefore, the enzyme reaction is affected by ph, solvent as well as temperature. To enhance biomass fuel production rate, optimization of the reaction condition and understanding of relationship between conformation of enzyme and enzyme reaction are important issues. For observation of the conformation of enzyme, high sensitive microscope is useful. Atomic force microscope is one of the scanning prove microscope, and it can observe the picture of small target less than a few μm. High speed atomic force microscope (Agilent 5500 AFM/SPM, Agilent) installed in MAL can observe not only the picture of the structure of materials, but also movie of the behavior in the liquid [18], the experimental procedure is shown in Fig. 8.

The high speed atomic force microscopy will be able to observe the conformation of enzymes in liquid. In addition, MIR-FEL will make the chemical bond of enzyme excite, and introduce the change of conformation. Therefore, we observe the change of conformation by MIR-FEL irradiation at real time. The different point between thermal excitation and excitation by MIR-FEL irradiation is that MIR-FEL can excite specific chemical bond of enzyme. Therefore, we can understand the relationship between conformation of enzyme and excitation of specific chemical bond, and we can control the conformation of enzyme by MIR-FEL irradiation.

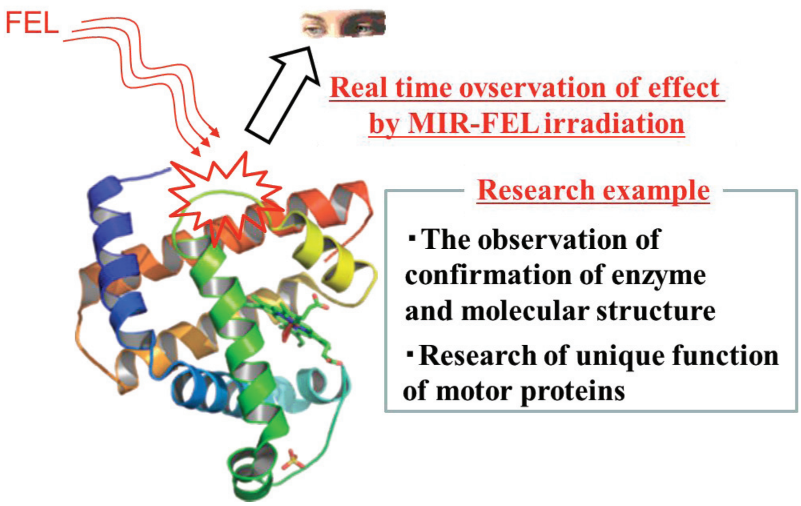

Fig. 8. Procedure of the microscopy system with MIR-FEL.

3. Conclusion

MAL in KU-FEL in Kyoto University has already constructed for contributing to energy science research. The six evaluation systems, a photoluminescence spectrometer, a photoelectron spectrometer, a high speed atomic force microscope, a high performance liquid chromatography mass spectrometer, a super centrifuge, and an ICP atomic emission spectrometer combined have constructed in MAL and the connection between the evaluation systems and MIR-FEL is under construction. The evaluation systems with MIR-FEL will aid the development of energy science by new scientific approach such as selective excitation of chemical bond. The MAL is open to use for worldwide users.

Acknowledgements

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