Graduate School of Advanced Science and Engineering
Waseda University

博 士 論 文 概 要
Doctoral Thesis Synopsis

論 文 題 目
Thesis Theme

In-situ analysis on interfacial nano-structures and reactions by using surface-enhanced Raman spectroscopy

表面増強ラマン分光法を用いた界面ナノ構造
および反応プロセスの in-situ 解析

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Chemistry of interfaces and surfaces play a key role in understanding numbers of diverse phenomena, such as chemical reactions, electrochemical processes, nanoparticle behavior, and so on. In-situ studies on these interfacial processes and depth profiling play an important role for properly addressing the issues of worldwide relevance, and for this, experimental methods, which discriminate interfacial structure with high resolution, are required. Raman spectroscopy is a powerful technique which can achieve in-situ observation of the molecular vibration. Nevertheless, it is known that some vibrations show weak Raman scattering so that micro constituents are difficulty to be observed by this approach. In these situations, surface-enhanced Raman spectroscopy (SERS) could be beneficial to enhance weak Raman signals and distinguish the vibration of a group or a chemical bond in the sample with low concentration. However, for the analysis of the interfacial reaction, SERS is not widely employed comparing to other traditional approaches, due to the confined SERS sensor to enhance the signals.

To advance the interfacial analysis, Raman spectroscopy and SERS were employed in this study to realize the analysis on several ultra-thin samples. The originality of this study is applying the SERS sensors and realizing in-situ and kinetic measurements on three types of nano-films, with high sensitivity and resolution. In addition, temperature calculation from anti-Stokes Raman scattering and depth profile with a step of 0.1 nm also support the interface analysis. The measurements and analyses were successfully expanded to various kinds of nano-film samples, including (3-aminopropyl)triethoxysilane derived self-assembled monolayers (APTES SAMs), single layer graphene (SLG), and the solid-electrolyte interface (SEI) films formed at the electrode surface of Li-ion battery (LIB). The application potentials of the SERS in thin-film materials and interfacial reactions were demonstrated via the measurement on some well-known structures, including the analysis on the phase transition, the accurate vertical structure and the two interfacial junctions of APTES SAMs, and the thermal stability of SLG. Furthermore, SERS was applied to characterize the SEI layers in LIB, including the kinetics of their formation, the depth profiling, and their generation mechanism focusing upon the species such as Li_2CO_3. The interfacial observation on the thin-film materials was completed with atomic resolution, high quality, kinetically and in-situ by using the SERS sensors.

This thesis consists of five chapters as follows.

Chapter 1 is the general introduction. It explains the motivation of entire study, the techniques employed, the target samples and the strategy in this study. Some fundamental concepts and theories about Raman spectroscopy, SERS, and anti-Stokes and Stokes Raman scattering are introduced. Moreover, some important supporting approaches composing the SERS sensor, the time-resolved measurement and the depth profile measurement are also explained in detail.

Chapter 2 demonstrates the ability of SERS in the interfacial analysis of nanoscale structures. Using SERS, the depth profiling was realized with atomic resolution and the in-situ kinetic observation was carried out on APTES SAMs and SLG. The originalities of the studies described in chapter 2 are firstly realizing the depth profile on ultra-thin sample in nanometer scale using SERS, firstly finding the phase transition point of APTES SAMs and the thermal stability of SLG under laser heating. (1) An ideal APTES SAMs on silica surface supposed to be monolayer, while the alignment of APTES moiety has been demonstrated to be not complete

order in actual preparation. For analyzing the internal structure, the sample APTES SAMs was deposited with Ag nanoparticles to enhance the Raman signals and to obtain subtle structure information. Combining with a plasmonic field gradient device, SERS was successfully employed to realize an accurate depth profile at atomic level, with depth resolution of 0.1 nm. As a result, it could distinguish the vertical Raman intensity variations of the vibrations from specific groups in APTES, such as Ag-N, NH_2, and Si–O, with atomic scale resolution. Moreover, some frequency shifts that occurred during the depth profiling were analyzed to discuss the bonding behaviors at the interfaces. From these results, it was indicated that not every APTES moiety was bonded with each other and bonded Si–O band existed at the same time, and that it is possible for the entire APTES moieties to bend such that the head and tail groups are oriented towards the substrate surface. (2) The demonstration was expanded to the in-situ kinetic observation on APTES SAMs by using SERS. The phase transition of APTES SAMs was analyzed using surface-enhanced anti-Stokes and Stokes Raman scattering. Ag nanoparticles were also deposited on APTES SAMs as SERS sensor. The time-resolved measurement was carried out to in-situ monitor the variation in the Raman peaks of APTES SAMs along with laser heating process. It was suggested that the structure of APTES SAMs changed from ordered to disordered around 118 °C. Thermal damage was primarily responsible for the variation in the O–Si–O, Si–C–C and carbon chain. The Si–O–Si bands, the bending vibration at Si–CH_2 and the NH_2 group still showed obvious SERS peaks after the phase transition. (3) The thermal stability and the defect generation of SLG subjected to confocal laser heating were studied in-situ, according to the anti-Stokes and Stokes Raman spectra. The thermal stability of SLG basal plane and edge plane was demonstrated to be different. The basal plane of SLG was found to be unstable above 500 °C, while the edge plane could not endure around 220 °C. The demonstration in Chapter 2 confirm the capacity of SERS for analyzing interfacial structure and reaction of thin film material with high resolution, in-situ and kinetically.

SERS was further applied to the interfacial analysis of LIB electrodes, to observe the important but unclear structure, the SEI films. The results are discussed in chapters 3 and 4. In chapter 3, the in-situ kinetic reaction at the graphite anode surface was discussed using SERS. The originalities of the studies discussed in chapter 3 are firstly applying transmission type SERS sensor in the observation of SEI films in LIB and firstly observing kinetic reaction during SEI formation with multi laser spot. The SEI film is known to be formed at the electrode surface due to the side reactions mainly caused by the reduction of electrolyte, and the quality of SEI film play an important role in the performance of batteries. For the two traditional electrolytes, PC-based electrolyte and EC-based electrolyte, there are controversies on the reaction at the electrode surface, especially the reason why the PC-based electrolyte cannot form effective SEI as EC dose. Therefore, understanding the actual nature and the composition of SEI films in these two types of electrolytes is of prime interest in this study. To compare these two electrolytes, two SEI films were formed in PC-based electrolyte and EC-based electrolyte during the first cycling of cyclic voltammetry. The in-situ kinetic measurements were conducted on SEI films along with laser heating, to identify their thermal stability. The results reconfirmed the formation of compact SEI films in EC-based electrolyte and loose one in PC-based electrolyte, corresponding to the previous reports. Moreover, in order to detect the kinetic Raman signals during the SEI formation, transmission-type SERS sensors and the 532

nm laser was used. As a result, Li_2CO_3 was detected as a product only in PC-based electrolyte, which could be the reason for the instability of the SEI films in the PC-based electrolyte. Furthermore, the real-time 2D mapping of the SEI formation was carried out by using the Raman microscopy installed with 11 x 11 multi-laser spots, which allows the simultaneous monitoring on a square area of sample surface and recording 121 Raman spectra in single measurement. For distinguishing the kinetic reaction on the basal and edge of graphite, HOPG was chosen to be the model electrode (anode), owing to the clear basal and edge plane. The Raman mapping results during SEI formation demonstrate that Li_2CO_3 product was formed mainly at the edge of HOPG, the Li_2CO_3 formation start around -900 mV and the organic products were formed from -1200 mv.

Chapter 4 further investigates the Li_2CO_3 formation, its relation with the adsorption behavior of electrolyte solvent species at the anode/electrolyte interface and its depth profile in the SEI films, by using SERS. The originalities of the studies in this chapter are firstly detecting Li_2CO_3 using SERS sensor, figuring out the correlation of Li_2CO_3 formation with interfacial molality of cyclic carbonate, and the depth profiling of the SEI film using the SERS sensors. From the results, Li_2CO_3 was further identified to be a product of PC-based electrolyte, by using 785 nm laser and a SERS sensor with Au nanoparticles. To explore the mechanism of Li_2CO_3 formation in PC-based electrolyte, Raman mapping studies were performed to elucidate the interfacial behavior of the PC and EC and its correlation with the Li_2CO_3 generation. The molalities of PC and EC at the graphite surface were found to be different. Molality of PC at the interface was lower than bulk sample, while the molality of EC at the graphite surface is similar to bulk sample and higher than PC. The results suggested that, comparing with EC, PC has poor adsorption ability than other co-solvent at the surface of graphite surface, possibly due to the loose PC-PC aggregates. Besides, when applying potential to the interface, the molality of PC is slightly elevated but still lower than EC. Moreover, using HOPG as the graphite model, the lower molality of PC was further demonstrated to occur at the edge of graphite only. The edge of graphite is the exact main reaction position for Li_2CO_3 formation. Therefore, the mechanism could be concluded that the low molality of PC at the edge of graphite may lead to the two-electron reduction at the interface and generate more Li_2CO_3 products. Finally, the depth profiling of the SEI film in PC-based electrolyte indicated that the Li_2CO_3 products may be embedded in organic layers to consist the outer layer of SEI. Chapters 3 and 4 demonstrate that SERS was successfully applied in the interfacial analysis of SEI films, using appropriate SERS sensors.

Chapter 5 is the general conclusion of this thesis. The results of analyzing nano-film materials were summarized. The advantage and shortage of SERS on observing interfacial reaction is concluded. Furthermore, the prospect of obtaining Raman scattering with higher resolution and sensitivity was described. The key point is to develop the SERS sensor which is available to higher enhancement factor. Using various types of SERS sensors, the analysis on diverse nano-film materials and interfacial reactions are expected to be realized with high resolution.

早稲田大学　博士（工学）　学位申請　研究業績書

(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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種 類 別 (By Type)	題名、　　発表・発行掲載誌名、　　発表・発行年月、　　連名者（申請者含む）(theme, journal name, date & year of publication, name of authors inc. yourself)
○　Paper	Estimated phase transition and melting temperature of APTES self-assembled monolayer using surface-enhanced anti-stokes and stokes Raman scattering, Applied Surface Science, 363, 572–577, 2016. Yingying Sun, Masahiro Yanagisawa, Masahiro Kunimoto, Masatoshi Nakamura and Takayuki Homma
○　Paper	Thermal stability of single-layer graphene subjected to confocal laser heating investigated by using in situ anti-Stokes and Stokes Raman spectroscopy, Electrochemistry, 2016 (In press) Yingying Sun, Masahiro Yanagisawa, and Takayuki Homma

早稲田大学　博士（工学）　学位申請　研究業績書

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Presentation	In-situ Raman spectroscopy study on the preferential adsorption of electrolyte species on electrode surface of Lithium ion battery, PRiME 2016/230th ECS meeting, E03-1596, Oct. 2016, Hawaii, USA, <u>Yingying Sun,</u> Masahiro Yanagisawa, and Takayuki Homma
Presentation	In-situ temperature measurements on the phase change point of monolayer APTES by Surface-enhanced anti-Stokes and Stokes Raman scattering, The 7th international symposium on surface science, Nov. 2014, Shimane, Japan, <u>Yingying Sun,</u> Masahiro Yanagisawa, Masahiro Kunimoto, Masatoshi Nakamura and Takayuki Homma
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Presentation	Study on chemical structure inside APTES SAMs by using SERS: depth profile and phase transition process, CSJ2015, Tokyo, Japan, <u>Yingying Sun,</u> Masahiro Yanagisawa, Masahiro Kunimoto, Masatoshi Nakamura and Takayuki Homma