Novel Plasmonic SERS Sensor and Its application to Chemical Analysis for Solid/Solid Interfaces

M.Yanagisawa[1], M.Saito[1], T.Homma[2]
1 Nanotechnology Research Center, Waseda University, 513, Wasedatsurumaki-cho, Shinjuku, Tokyo 162-0041, Japan
Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo 169-8555, Japan

1. Introduction

A chemical analysis for buried interfaces has become important since there have been increased devices, such as Li ion batterys, LEDs, solar cells, etc. with liquid/solid, liquid/liquid, or solid/solid interfaces. Unfortunately, analytical means are so limited compared with that of surface analysis such as XPS, TOF-SIMS, and so on. Raman scattering spectroscopy with a confocal microscope is a useful method to analyze multilayers [1]. However, a depth resolution is an order of micrometer. We have developed a Surface-Enhanced Raman Scattering (SERS) sensor with a plasmon antenna [2] and demonstrated the analysis near the liquid/solid interface with a depth resolution of nanometer [3]. In this report, we demonstrate a new type of plasmonic SERS sensor with a depth resolution of sub-nanometer and its application to the chemical analysis for the solid/solid interface.

2. Experimental

Our SERS sensor is a transmission type as shown in Fig.1. Ag nanoparticles (b) with a diameter around 30 nm were evaporated onto a convex lens (a) composed of fused quartz. An excitation light, wavelength of 532nm, is irradiated through the sensor which is put on a sample. Depth profile images of Raman spectra were acquired by displacing a focus position with a piezoelectric actuator.

3. Results

Figure 2 shows a depth image of G-band intensity for Highly Ordered Pyrolytic Graphite (HOPG). Periodical crystal structure is observed in which the periodic distance, 0.3nm, showed good agreement with the layer distance, 0.335 nm. Some disturbances in the periodical image at around the surface are observed near a step, where a measurement laser beam is traversed. Atomistic depth resolution is obtained with a steep electric field, enhanced by a localized plasmon.

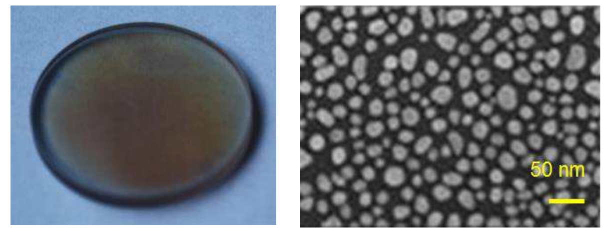
Figure 3 shows the Raman spectrum of SiC, observed at around the interface between a diamond-like carbon (DLC) film, fabricated by plasma CVD, and a Si substrate. Thickness of the interlayer is around 1 nm or less (Fig.4).

Acknowledgments

This research was partially supported by "Nanotechnology Network Project", "Development of Systems and Technology for Advanced Measurement and Analysis", and "Grant-in-Aid for Scientific Research, 23656470 and 25630041" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] M.P.Miguel and J.P.Tomba, Prog.Org.Coat., **74**, 43 (2012).
[2] M. Yanagisawa, N. Shimamoto, T. Nakanishi, M. Saito, and T. Osaka, ECS Trans., **16**, 397 (2008).
[3] B.Jiang, T.Ouchi, N.Shimano, A.Otomo, M.Kunimoto, M.Yanagisawa, and T.Homma, Electrochim.Acta, **103** (2013) in press.



(a) Convex substrate (b) SEM image of Ag nanoparticles

Fig.1 (a) Transmission-type plasmonic SERS sensor on which (b) Ag nanoparticles are evaporated.

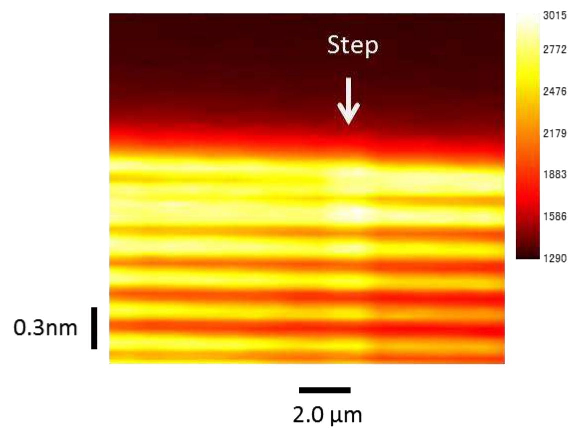


Fig.2 Raman depth image of G-band intensity for HOPG.

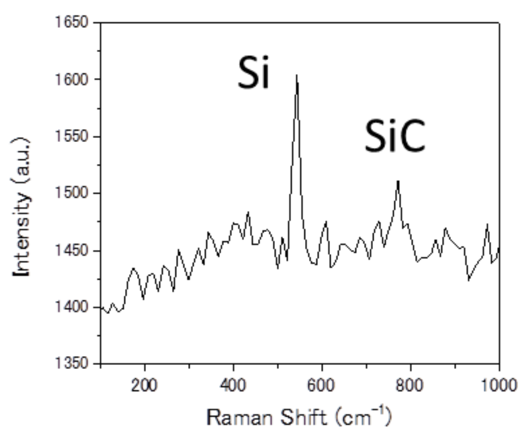


Fig.3 Raman spectrum at DLC/Si interface.

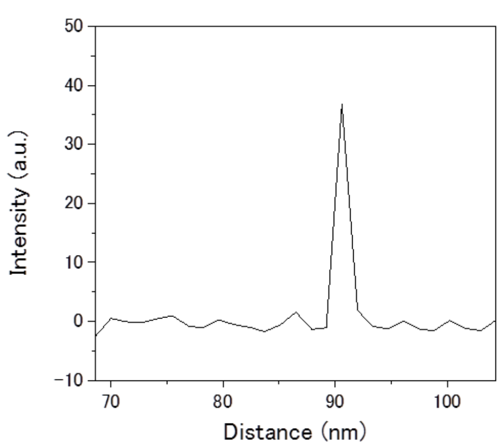


Fig.4 Depth profile of Raman intensity for SiC.