Several surface-analytical devices utilizing surface-enhanced Raman scattering (SERS) have been developed since the first observation of the enhancement of Raman signals from pyridine adsorbed onto a Ag electrode of sub-micrometer scale.\(^1\) Some of these devices are based on the so-called SERS substrate,\(^2\) in which plasmonic metal films, i.e., Au or Ag, are coated on a patterned substrate composed of Si or quartz glass. These devices are utilized for gas sensing or the analysis of molecules adsorbed onto plasmonic metals. As an example of such a device, researchers have reported on nanofabricated devices with coaxial groove patterns (plasmon antennas) that can detect small amounts of gas molecules at the ppb level.\(^5\) Furthermore, such a device has been used to reveal the layered molecular features of hypophosphite/hydrazine on a Cu surface in water solution.\(^7\)–\(^9\) However, measurement has thus far been limited to SERS substrates composed of plasmonic metals. Meanwhile, it has been reported that the coatings of nanoparticles of plasmonic metals on analyte surfaces can be utilized to analyze the chemical structure of sample surfaces with high sensitivity.\(^10\)–\(^12\) However, this method can be categorized as destructive sampling, which is applicable for in situ measurements, such as kinetic measurements of the sample surface. In this context, tip-enhanced Raman spectroscopy (TERS)\(^16\) has been proposed to obtain Raman images of surface topographies with high lateral space resolution. However, TERS is limited to the measurement of highly “Raman-active” materials because its low sensitivity is reciprocally related to high spatial resolution. In TERS, a single hot spot with a Raman-enhanced area is located on the tip (diameter of around 30 nm) of a needle coated with plasmonic metal. Therefore, the enhancement factor (EF) is not so large, approximately $10^6$, compared with a dimer particle with plasmonic coupling (EF of $10^5$ or $10^6$).\(^{16}\) In addition, the system is expensive because it requires the use of a scanning probe microscope (SPM), i.e., an atomic force microscope (AFM) or scanning tunneling microscope (STM) in conjunction with the Raman spectrometer.

In this context, in our study, we developed a new analytical SERS device that enables us to measure the chemical structure of a given surface with high sensitivity. Our setup affords ease of use and allows the nondestructive investigation of samples. Furthermore, our device is inexpensive, does not require any additional devices, and does not place restrictions on the type of substrate materials. Figure 1(a) shows the optical image of our device, a transmission-type plasmonic sensor (TPS), composed of a planoconvex quartz glass substrate of 20 mm diameter, 92 mm curvature radius, and 2 mm thickness, on which Ag is deposited by sputtering under the following deposition conditions: deposition rate of 5 nm/min, Ar pressure of 0.67 Pa, and background pressure of $5 \times 10^{-4}$ Pa. The average thickness of the Ag film can be precisely controlled by adopting a slow deposition rate of 5 nm/min. Good reproducibility was achieved for the shutter speed of 1 s, which corresponds to the thickness reproducibility of 10%. No adhesion layer, such as a Cr layer, is deposited for an underlayer of Ag because it absorbs surface plasmons. Furthermore, islandlike Ag nanoparticles (NPs) are retained unless they are rubbed. The Ag film is deposited in the form of islandlike structures on the substrate, which makes the structure con-
ducible to generating surface plasmons, as shown in Fig. 1(b). The structure is formed via the balance of the surface energy (wettability) between Ag and the quartz surface in the initial stage of Ag growth during the sputtering. Figure 1(c) shows the statistical distribution of the diameter of the Ag nanoparticles (NPs) on the substrate. Here, we remark that because the interparticle distance also exhibits a statistical distribution, the diameter range corresponding to the maximum Raman enhancement can be selected by adjusting the sputtering conditions (described later). Figure 1(d) shows the cross-sectional transmission electron microscopy (TEM) image of “dropletlike” Ag NPs on the SiO2 substrate. Here, note that the contact area between the Ag NPs and the SiO2 substrate plays an important role in the analysis of the sample surface (Fig. 2). Next, by the finite-difference time-domain (FDTD) method (RSoft Design Group Fullwave), we calculated the electromagnetic field around (a) an isolated Ag NP (diameter of 30 nm) and (b) a dropletlike Ag particle sandwiched between SiO2 surfaces when subjected to 532 nm excitation light incident perpendicular to the NP surface. The plasmonic field of the isolated Ag NP was observed to be polarized parallel to the electric field of the incident light beam, as shown in Fig. 2(a). However, strong plasmonic fields appeared at the substrate (SiO2)/Ag NP interface and the Ag NP/sample (SiO2) interface; these fields are perpendicular to the electric field of the incident light (along the propagated direction), as shown in Fig. 2(b). This result is important for analyzing the sample surface because Raman scattering is enhanced in large plasmonic fields, wherein the Raman intensity is proportional to the fourth power of the electric field. The calculated electric fields (E) at hot spots, normalized by an incident light source, are 2.3 for isolated Ag NP and 4.2 for sandwiched Ag NP, respectively. The electric field of 2.3 agrees with that of a single Ag NP.22) Although the electric field of 4.2 per hot spot is not so large compared with that of the Ag NP dimer,22) the fourth power of the summed enhanced electric field in a laser spot, wherein a number of effective (contributing to the enhanced signal) Ag NPs (around 40) exist, is 12000, which agrees approximately with the Raman enhancement of 15000 times, as shown in Fig. 5(a). Moreover, it is possible for the TPS to efficiently collect scattered Raman signals from incident light focused on the sample through an objective lens. On the other hand, with a TERS system, it is difficult to focus light on the small area of the tip with a high-NA objective lens because the excitation light irradiates the tip along an inclined direction to generate the vertical component of the electric field. Furthermore, the collection efficiency of the scattered Raman signal is not very large because of signal interference with the AFM cantilever.

Figure 3 schematically illustrates the measurements obtained with the TPS, which is placed onto the sample surface that comes into contact with the Ag NPs. A laser beam is focused at the Ag NPs/sample interface through the rear surface of the TPS. The contact area (diameter of 50 µm) is observed to correspond to the zeroth-order Newton ring, wherein the laser beam (around 5 µm in diameter) is precisely incident at the center of the contact area. The plasmonic field exponentially decays from the surface along the depth direction of the sample. The calculated 1/e-decay depth is 3 nm for a laser-beam wavelength of 532 nm. This result indicates that the enhanced Raman spectrum is acquired from the subsurface of the samples. For a setup with a 532 nm laser beam and 10× objective lens, several Ag NPs (around 130) exist in the beam’s waist spot (diameter of 1.13 µm). The proportion of the “effective” Ag NPs (contributing to the enhanced signal) with a diameter of 30 nm is around 29%, as determined by image analysis of SEM observations (described later). This result indicates that the deposition of uniform NPs via nanofabrication processes such as electron beam (EB) lithography or the focused ion beam (FIB) technique may afford improved sensitivity. However, our sensor is inexpensive precisely because it is fabricated via a simple dry-deposition process, i.e., sputtering or vacuum evaporation. Furthermore, a simple dry process is suitable to prevent sample contamination since SERS devices exhibit extremely high sensitivities; the use of complicated fabrication processes can cause contamination, leading to wrong analytical results in measurements.
Next, we consider the optimization of the Ag-NP diameter, keeping in mind that Raman enhancement is sensitive to the NP shape. In our study, we examined the sensitivity of our TPS with the use of a diamond-like carbon (DLC) film (thickness of 2 nm) on a CoPt alloy film for hard-disk application. Figure 4(a) shows the Raman intensity of the G-peak, NP diameter, and distance between the NPs as functions of the average thickness of the deposited Ag. The maximum Raman intensity is observed for an NP diameter of 30 nm and an interparticle distance of 20 nm, the results of which were processed by image analysis of the Ag NPs with the use of a software tool (Image Metrology SPIP). The standard deviation (error bar) of the NP diameter and interparticle distance increases above the average thickness of 6 nm, corresponding to decreased Raman intensity, because particles tend to aggregate beyond this thickness (as can be observed via SEM imaging), and subsequently, the plasmonic resonant effect weakens. The effect of the Ag layer thickness can be examined from the perspective of the observed spectral shapes in the absorption spectra for the sandwich configuration of SiO$_2$/Ag-NP/SiO$_2$, as shown in Fig. 2(a), wherein the maximum intensity of the plasmon absorption band is observed at an average thickness of 5 nm [corresponding to maximum plasmonic resonance, Fig. 4(b)]. The resonant wavelength (peak position) shifts from 500 to 508 nm with increasing average thickness. Furthermore, the absorption spectral peak extends to the long wavelength range for samples with thicknesses of 6 and 7 nm, and the intensity of the absorption band again increases at around 800 nm. These spectral changes correspond to changes in the particle configuration. According to an early report$^{23}$, a resonant absorption was observed at around 380 nm for a Ag sphere (diameter of 60 nm). On the other hand, the resonant peak appeared at 508 nm for the sandwiched Ag NP (diameter of 30 nm). They also showed that the redshift occurs for a sinking Ag sphere in mica as a function of contact area. Therefore, the reason why the resonant wavelength of the sandwich configuration is longer than that of the isolated Ag NP is considered to be the effect of the contacted dielectric material.

Next, Raman spectra were acquired with the use of a Raman spectrometer (Tokyo Instruments Nanofinder 30) equipped with a confocal microscope. The spectrometer specifications were as follows: Nd:YAG laser (532 nm, 0.6 mW), acquisition time of 1.0 s, grating with 600 grooves/mm, and pinhole size of 50 µm. The performance of our TPS is shown in Fig. 5. The enhanced Raman intensity of the

![Fig. 4](image1.png)

**Fig. 4.** (a) Diameter and interparticle distance with average (filled circles) and standard deviation (error bars) as functions of average Ag thickness, and (b) absorption spectra for various values of average Ag thickness.

![Fig. 5](image2.png)

**Fig. 5.** (a) Raman spectra of undoped DLC film (thickness of 2 nm) with and without sensor, and (b) enhanced Raman spectrum of N-doped DLC film (doped layer of 0.7 nm). Other than the D- and G-peaks, peaks (*) assigned to N-embedded carbon are also observed in the enhanced Raman spectrum. (c) Typical molecular model of NH stretching vibration in sp$^3$ carbon network observed at 498 cm$^{-1}$, wherein arrows indicate the directions of vibration.
G-peak at around 1550 cm$^{-1}$ for an undoped DLC film (thickness of 2 nm) with the TPS (red line) is $>15,000$ times (after subtracting the background) that of the normal Raman spectrum (blue line), as shown in Fig. 5(a). In the SERS spectrum of the DLC film, we observe small peaks that can be assigned to a small amount of organic materials; these correspond to decomposed by-products of the source gas (ethylene) in the chemical vapor deposition (CVD) process. The EF is estimated to be $5.6 \times 10^5$ for a calculated hot-spot size of 3 nm on a Ag particle of 30 nm diameter [Fig. 2(b)].

The EF value is sufficiently large for the isolated particle when compared with the EF of the order of $10^8$ for coupled particles with gaps $<1$ nm in which plasmonic resonance occurs. Figure 5(b) shows the enhanced Raman spectrum of the DLC film with a nitrogen-doped layer (thickness of 0.7 nm) present near the surface of the DLC film. Other than the D- and G-peaks originating from the carbon network, several small peaks assigned to nitrogen carbon bonding are also observed. These peaks show good agreement with the Raman spectra assigned to NH bonding embedded in sp$^2$ and sp$^3$ carbon networks composed of molecular models calculated by the density functional theory (DFT) method (Gaussian 09 package) with the function (B3LYP) and the basis set (6-31G**).

Our TPS is also applicable with liquid/solid interfaces because a vacuum environment is not required for TPS operation. Furthermore, the Raman spectral intensity of liquid molecules at the defocused position is negligibly small in comparison with the strong enhancement at the interface (on which the laser beam is focused) because the penetration depth of the plasmonic field is very small (a few nanometers). Furthermore, the TPS enables nondestructive in situ measurements of kinetic changes in surfaces or interfaces. Moreover, in combination with time-resolved Raman acquisition, the TPS can be used to observe chemical structural changes occurring as a result of energy perturbations arising from electronic, thermal, mechanical, magnetic, and electromagnetic energies.

Our device is a highly versatile surface-analytical tool because it offers the advantages of nondestructive characterization, ease of handling, low-cost fabrication, and high sensitivity. The TPS is suitable for applications such as the quality inspection of industrial products and in academic research areas concerning energy devices (batteries, solar cells), storage devices (hard disks/optical disks), mechanical devices (engines, bearings), and biomedical applications (cell membrane analysis, metabolism).

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