

AN OPTICAL METHOD TO DETECT AMOUNT OF PARTICLES DEPOSITED ON A SUBSTRATE

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Key Words: Particle Deposition, Clean Surface, Reflectometry, Laser Beam, Measuring Apparatus

It is examined whether the principle of reflectometry, developed to measure the thickness of a thin layer on a surface, is applicable to detecting quantitatively the amount of fine particles deposited on a substrate. It is found that the relative difference of parallel and perpendicular components of the laser beam reflected on the surface is proportional to the particle coverage if experimental conditions are suitably selected, and that this principle is able to be used to detect with high sensitivity *in-situ* the amount of particles.

Introduction

It is important in many processes of advanced technology to detect *in-situ* the amount of deposited particles or the thickness of thin films on a substrate quantitatively and non-destructively. As for film thickness, measuring methods which satisfy the above conditions are optical, such as total internal reflection fluorescence (TIRF)^{6, 7, 8)}, ellipsometry^{1, 4, 10)} and reflectometry^{2, 3, 5)}. TIRF can produce real-time data, but the substrates and adsorbates which one can use are limited, because the substrates must be transparent and the adsorbates must be either intrinsically fluorescent or be labeled with a suitable fluorophore. In the case of ellipsometry and reflectometry, the film thickness is evaluated by the change of polarization of the light reflected on a sample surface. In ellipsometry, the refractive index of the film is also evaluated, although it normally takes time to obtain the data. In reflectometry, the film thickness is measured instantaneously and it is important to note that the measuring principle is simple and the apparatus is easy to make.

In the case of deposited particles, either a microscope or a scanning electron microscope has been employed to evaluate the size and amount of deposited particles, but it is apparently not an *in-situ* measurement. In the present study, whether the principle of reflectometry is applicable to measure *in-situ* a small amount of the fine particles deposited on a substrate quantitatively or not is examined experimentally.

1. Measuring Principle

When polarized incident light is reflected off a flat surface as illustrated in Fig. 1, the polarization will be altered. Since this change of polarization depends on the surface characteristics, the change may be employed to

evaluate the amount of particles deposited on a substrate.

The light reflected on a surface is divided into the parallel and perpendicular polarization components with respect to the plane of incidence. The reflected amplitudes E_p and E_s are correlated with those of the incident light, E_{p0} and E_{s0} , as follows. Here we denote parallel and perpendicular polarization components as *p* and *s* respectively.

$$E_p = r_p E_{p0} \quad (1-a)$$

$$E_s = r_s E_{s0} \quad (1-b)$$

where r_p and r_s are the amplitude reflectivities. Then the intensities of reflected light I_p and I_s are given as follows,

$$I_p = |E_p|^2 = R_p I_{p0} \quad (2-a)$$

$$I_s = |E_s|^2 = R_s I_{s0} \quad (2-b)$$

where $I_{p0} (= E_{p0}^2)$ and $I_{s0} (= E_{s0}^2)$ are the incident intensities and $R_p (= r_p^2)$ and $R_s (= r_s^2)$ are the energy reflectances. The difference of reflected intensities normalized by the sum of the intensities, S , is defined as:

$$S = \frac{I_p - I_s}{I_p + I_s} = \frac{R_p - fR_s}{R_p + fR_s} \quad (3)$$

where $f = I_{s0}/I_{p0}$. This equation is applicable to a surface with deposited fine particles, as well as a surface without particles. In the case of a surface with particles, the intensity of light detected is averaged over the contribution of the light from the bare surface and deposited particles. The difference of S -values between a clean surface and a surface with particles is given by

$$\Delta S = S_2 - S_1 \quad (4)$$

where we denote the surfaces without and with deposited particles as 1 and 2, respectively. Since the magnitude of

* Received on October 24, 1994. Correspondence concerning this article should be addressed to K. Higashitani.

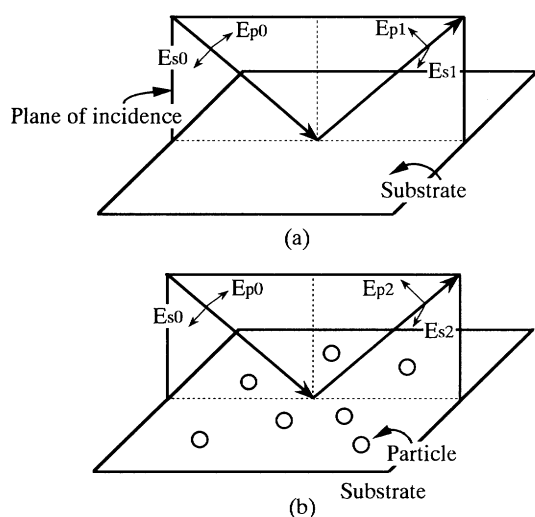


Fig. 1 Schematic illustration of light reflection and surfaces (a) clean surface (b) surface with particles

Table 1 Physical properties of deposited particles

	Particle diameter, D_p [μm]	Refractive index, n [-]
PSL	0.171	1.60
	0.436	
	0.714	
	1.14	
Silica	0.50	1.46

f is able to be altered by changing the incident polarization, one can choose the incident polarization such that $S_1 = 0$ where the relation $f = I_{s0}/I_{p0} = R_{p1}/R_{s1}$ holds.

$$\Delta S = S_2 = \frac{R_{p2} - fR_{s2}}{R_{p2} + fR_{s2}} \quad (5)$$

Then the magnitude of ΔS becomes a measure of the amount of deposited particles if the magnitude of S_1 for the clean substrate is chosen to be zero.

2. Experimental

2.1 Materials

The monodispersed polystyrene latex (PSL) and silica particles used are summarized in **Table 1**. Their diameters D_p were measured by photon correlation spectroscopy. A silicon wafer supplied from Shinetu Handoutai Co., Ltd. was used as the substrate. The substrate with deposited particles was prepared by attracting particles to the substrate electrostatically. Since the surface of the silicon wafer is negatively charged in pure water as well as PSL and silica particles, the charge of the wafer surface is changed to positive as follows⁹. After soaking the wafer into a 5% solution of a silane coupling agent, 3-amino-propyl triethoxysilane, and conducting a condensation reaction with SiO_2 on the surface layer, the wafer was rinsed with water and dried at 100°C . The positive charge of the surface was confirmed by observing the uniform deposition of particles on the surface.

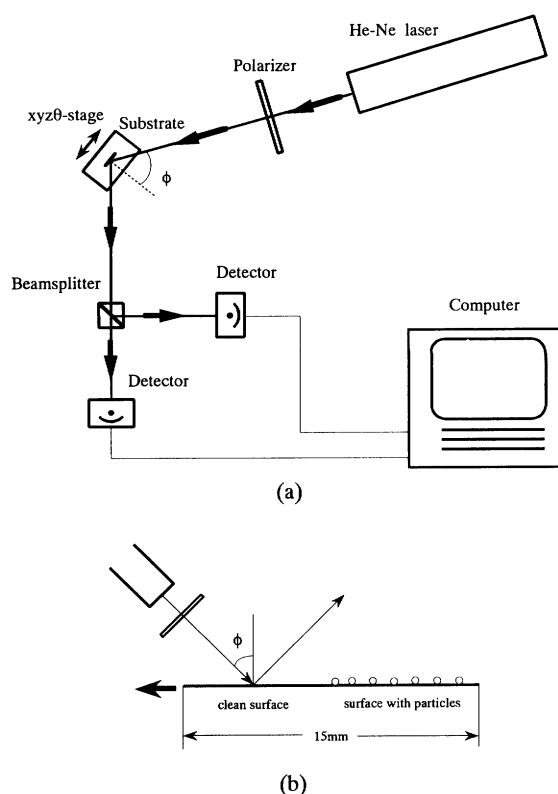


Fig. 2 Experimental apparatus. (a) Schematic illustration of experimental setup. (b) Details of laser beam and substrate

The modified wafer of $15 \times 15\text{mm}^2$ was dipped halfway into a suspension of particles to prepare a specimen with the upper half having a clean surface and the lower half having a surface with deposited particles. Surface particle coverage was controlled by changing the concentration of suspensions and the dipping time of the wafer. Then the specimen was rinsed with water and freeze-dried to prevent the particles from agglomerating. Coverage θ is defined as the fraction of the total cross section area of deposited particles against the area of the substrate. Since particles are monodispersed and spherical, the value of θ is calculated from the data on the number of deposited particles and their sizes, which are evaluated using a scanning electron microscope.

2.2 Experimental setup

The experimental setup is shown schematically in **Fig. 2(a)**. All optical equipments are fixed magnetically on a horizontal flat steel bed. A silicon wafer was fixed on a $\text{xyz}\phi$ -stage with a given incident angle ϕ , where the illuminated point on the sample could be varied without changing the incident angle by traveling the stage parallel. The light source employed was a He-Ne laser beam with wavelength = 632.8nm whose diameter was about 1mm . The incident laser was polarized in such a way that $S_1 = 0$ as explained above. The reflected light was split into parallel and perpendicular components by a beamsplitter and their intensities were detected by photon detectors. The value of ΔS defined by Eq. (5) was then calculated by the

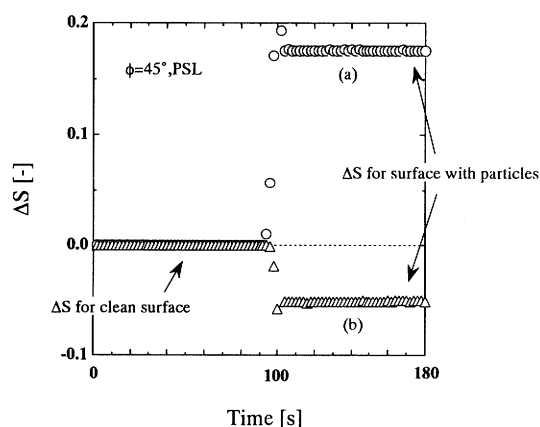


Fig. 3 Examples of ΔS -measurements. (a) $D_p = 0.436 \mu\text{m}$, $\theta = 0.216$ (b) $D_p = 1.14 \mu\text{m}$, $\theta = 0.120$

on-line computer.

2.3 Procedure

The incident laser was set to illuminate at the center of the side of the wafer with clean surface at a given incident angle ϕ ($30^\circ \leq \phi \leq 65^\circ$), as shown in Fig. 2 (b), and then the incident polarization was adjusted by the polarizer such that $S_1 = 0$. After the laser beam was kept standing for 100 seconds, the illuminated point was quickly changed to the center of the side of the wafer with deposited particles by traveling the stage parallel. Then the value of ΔS was calculated by the computer. The beam was kept standing at the same position for another 80 seconds.

3. Results and Discussion

Figure 3 shows the typical variation of ΔS at the clean and deposited surfaces against the illumination time of the laser. It is clear that the noise level of the reflected light is very low and the ΔS -value changes abruptly and largely at 100 seconds when the illumination point of the laser is changed. This indicates that the ΔS value can possibly be used as a sensitive measure of deposited particles. But it is interesting to note that the value of ΔS is not only positive as shown in Fig. 3 (a), but also negative as in Fig. 3 (b). Hence ΔS may depend on experimental conditions in a complicated way. Here we examine the dependence of ΔS on various experimental conditions to clarify whether the ΔS -value can be employed to evaluate the amount of deposited particles quantitatively.

The dependence of ΔS on the incident angle ϕ for various particle diameters is examined as shown in **Fig. 4**. For $D_p \leq 0.436 \mu\text{m}$, the value of ΔS , that is, the sensitivity of measurement, increases linearly with the incident angle, but the measurement becomes too sensitive and unstable at $\phi > 65^\circ$. The ΔS -value for $D_p = 0.714 \mu\text{m}$ varies in a very complicated way, and that for $D_p = 1.14 \mu\text{m}$ even becomes negative. The features appearing in the case of large particles are probably due to their complicated scattering characteristics. However, since these values are stable and reproducible, the ΔS -value can be employed as a measure of deposited particles.

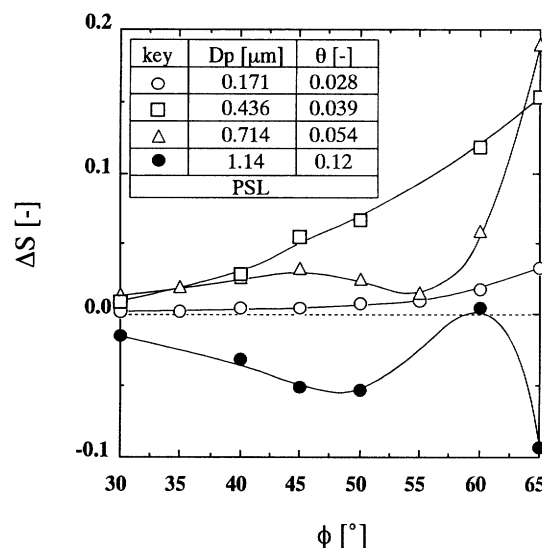


Fig. 4 Dependence of ΔS on incident angle for four particle diameters

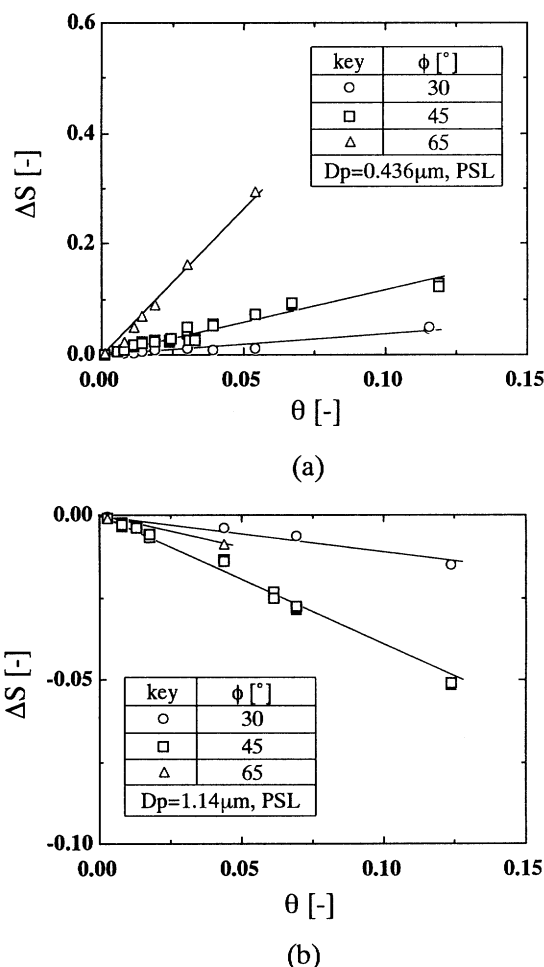


Fig. 5 Dependence of ΔS on coverage for three incident angles. (a) $D_p = 0.436 \mu\text{m}$, PSL (b) $D_p = 1.14 \mu\text{m}$, PSL

The dependences of ΔS on the coverage θ for $D_p = 0.436$ and $1.14 \mu\text{m}$ are examined as shown in **Fig. 5**. It is found that there exists a linear relation between ΔS and θ in the limited region of θ . ΔS for $D_p = 0.436 \mu\text{m}$ increases

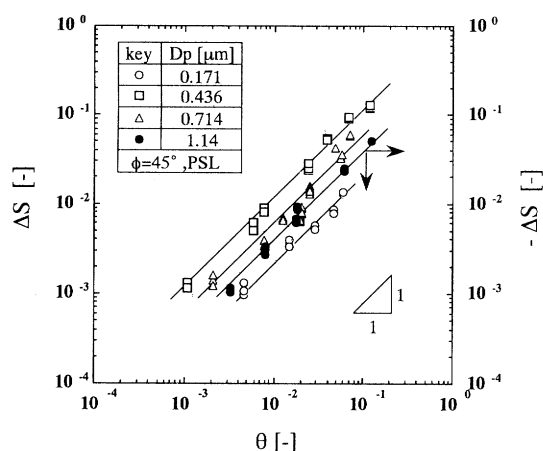


Fig. 6 Dependence of ΔS on coverage for four particle diameters

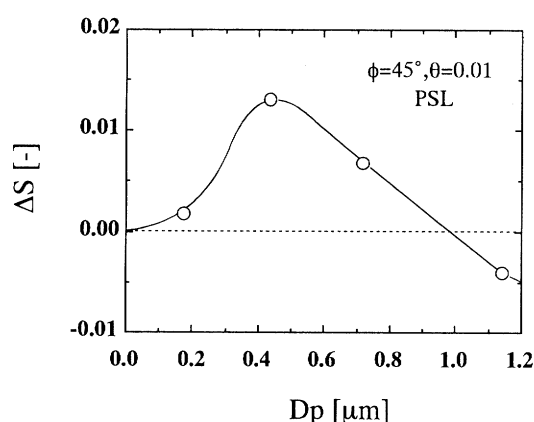


Fig. 7 Dependence of ΔS on particle diameter

with increasing value of ϕ as expected from the data in Fig. 4. It is interesting to note that the linear relation holds even for negative values of ΔS for $D_p = 1.14 \mu\text{m}$ as shown in Fig. 5. These data imply that ΔS has a high sensitivity and a wide linear region at $\phi = 45^\circ$. Hereafter the data at $\phi = 45^\circ$ are employed.

Figure 6 shows the dependence of ΔS on θ for various particle diameters on a double-logarithmic scale, where the values of $(-\Delta S)$ for $D_p = 1.14 \mu\text{m}$ are also plotted in the same figure. It is clear that the absolute value $|\Delta S|$ is proportional to particle coverage irrespective of particle size, but only in the limited region. The lower limit of $|\Delta S| = 10^{-3}$ is of the same order of the noise intensity so the lower limit is attributed to noise in the measurement. The measurement is also limited within $\theta \leq 10^{-1}$, and it is found that ΔS depends on θ in a very complicated way at $\theta \geq 10^{-1}$ for particles of any size. This non-linearity at $\theta \geq 10^{-1}$ is considered to be caused by multiple scattering of neighboring particles deposited on the surface. Hence it is concluded that the amount of deposited particles can be evaluated quantitatively at $\Delta S \geq 10^{-3}$ and $\theta \leq 10^{-1}$.

Figure 7 shows the dependence of ΔS for $\theta = 0.01$ on particle diameter. It is interesting to note that the value of ΔS has a maximum around $D_p = 0.4 \mu\text{m}$ and becomes negative for large particles. This feature is attributable to

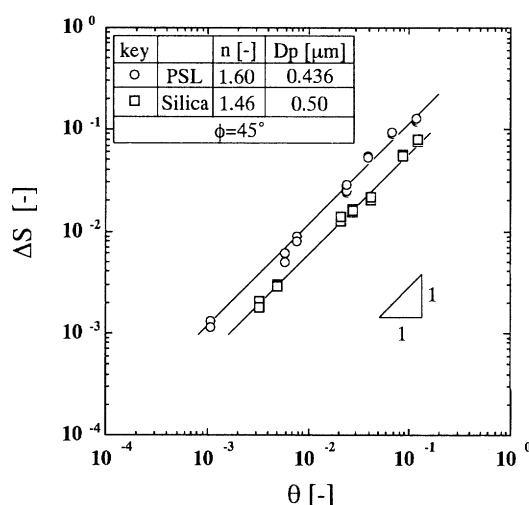


Fig. 8 Comparison of ΔS vs. θ between PSL and silica particles

the complicated dependence of the light scattering of particles on D_p . The result indicates that the measurement of ΔS becomes insensitive at $D_p \leq 0.1 \mu\text{m}$ and $D_p \approx 0.95 \mu\text{m}$. Therefore, there is a need to find proper experimental conditions when using this method.

The dependence of ΔS on θ for silica particles is compared in **Fig. 8** with that for PSL particles which have different properties but are similar in size. The relation of ΔS vs. θ is linear as expected. The reason why the value of ΔS is smaller in the case of silica particles is that the smaller refractive index than that of PSL particles makes the change of polarization of silica particles smaller.

Conclusion

Whether or not the principle of reflectometry can be used to detect the amount of fine particles deposited on a substrate or is examined experimentally. It is found that the relative difference of parallel and perpendicular components of reflected light on the surface with deposited particles is a sensitive measure to detect the amount of particles, although limitations exist for measurement, which depends on particle size, particle refractive index, coverage of particles and incident angle of light.

Nomenclature

D_p	= particle diameter	[m]
E^p	= amplitude of electric field	[V/m]
f	= I_{st}/I_{p0}	[-]
I	= intensity of light	[J/s·m ²]
n	= refractive index	[-]
R	= energy reflectivity	[-]
r	= amplitude reflectivity	[-]
S	= reduced degree of polarization	[-]
ΔS	= difference of reduced degree of polarization	[-]
ϕ	= incident angle of light	[-]
θ	= coverage of particles	[-]

<Subscripts>

p	= parallel polarization component with respect to a plane of incidence
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- s = perpendicular polarization component with respect to a plane of incidence
- 0 = incident
- 1 = reflected on a clean surface
- 2 = reflected on a surface with particles

Literature Cited

- 1) Beaglehole, D. : *Rev. Sci. Instrum*, **59**, 2557 (1988)
- 2) Dijt, J. C. , M. A. Cohen Stuart, J. E. Hofman and G. J. Fleer: *Colloids Surfaces*, **51**, 141 (1992)
- 3) Elgersma, A. V. , R. L. J. Zsom, J. Lyklema and W. Norde: *Colloids Surfaces*, **65**, 17 (1992)
- 4) Erman, M. and J. B. Theeten: *J. Appl. Phys*, **60**, 859 (1986)
- 5) Eurpatent Application No.88200230.6
- 6) Hlady, V and J. D. Andrade: *Colloids Surfaces*, **32**, 359 (1992)
- 7) Lok, B. K. , Y. L. Cheng and C. R. Robertson: *J.colloid Interface Sci*, **91**, 104 (1983)
- 8) Parsons, D. , R. Harrop and E. G. Mahers: *Colloids Surfaces*, **64**, 151 (1992)
- 9) Philipse, A. P. and A. Vrij: *J.colloid Interface Sci*, **128**, 121 (1989)
- 10) Reiter, R. , H.Motschmann, H. Orendi, A. Nemetz and W. Knoll: *Langmuir*, **8**, 1784 (1992)