

Determination of the Optical Functions of Various Liquids by Rotating Compensator Multichannel Spectroscopic Ellipsometry

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Rotating compensator multichannel spectroscopic ellipsometry has been employed to determine the optical functions of various liquids used in chemistry. We attempted three different measurement configurations: (1) air-liquid interface, (2) prism-liquid interface, and (3) liquid-sample interface. In prism-liquid interface, we found that the prism surface had roughness and it should be considered in analysis for accurate results. In liquid-sample interface, we had much higher reflection, better sensitivity, and less limitation compared to the other two configurations when crystalline silicon was used as reference sample. We discuss the merit of each configuration and present the optical functions of various liquids. Also we demonstrate Bruggeman effective medium theory to determine the optical properties of mixed liquid.

Key Words : Spectroscopic ellipsometry, Liquid refractive index

Introduction

Spectroscopic ellipsometry (SE) has been employed to study thin film growth or modification of surface in various liquid environments through *in-situ* or real-time measurements.¹⁻⁵ In SE, the change of polarization states upon reflection from surface is analyzed using various optical models. The desired parameters such as roughness, thickness, or volume fractions of materials can be deduced from the optical model when the optical constants of materials are provided for analysis. When SE measurement is performed on sample in liquid, one needs to provide the optical constant over wavelength, or equivalently optical function of liquid as an ambient in the model. One may use optical constant at single wavelength at 589.3 nm, namely refractive index, for spectroscopic analysis assuming same constant over wavelength. This is possible, because the dispersion is not severe in most liquids.

For accurate analysis, however, we need to provide the optical function of solution or solvent used in chemical process. We may refer to literature but usually it is not always possible to find optical constants over certain wavelength range.⁶ Moreover, when we work on new liquids whose optical constants are not known or mixed liquid at different concentrations, we have to figure them out by ourselves. Especially when measurements are performed at other than room temperature, the optical functions of almost all materials should be obtained by users including liquid, film, and substrate. This is because the optical functions are dependent on temperature.⁷

Optical constant for a single wavelength can be determined by the traditional methods such as refractometer or beam deviation.^{8,9} However, for optical functions, spectroscopy techniques are more effective if high accuracy is not required such as thickness measurement. In this study, we investigated simple methods to determine the optical

functions of liquids by SE. Formerly, rotating polarizer ellipsometry (RPE) or rotating analyzer ellipsometry (RAE) was popular due to its simple operation principle.¹⁰⁻¹² Recently, however, rotating compensator ellipsometry (RCE) is drawing more attention, because RCE has many merits over RPE or RAE.¹³⁻¹⁵ First, as analyzer or polarizer is fixed during measurements, any error related to the polarization sensitivity of detector or residual polarization of source can be eliminated. Second, the sensitivity for the linearly polarized reflection is much higher than RPE or RAE. This is very important feature when we measure the surface of liquid. Also, the sign of and the degree of polarization can be determined.

In this work, we attempted three approaches to measure the optical parameters of various liquids with spectroscopic RCE. Among them, liquid-sample interface is our proposed configuration to determine the optical properties of liquid. Also Bruggeman effective medium theory was introduced to study the optical properties of mixed liquid.

Experimental Section

Reagents and Materials. Reagent grade toluene, ethanol, methanol, methylene chloride, chloroform, ethyl acetate, hexane, tetrahydrofuran, ether, dimethyl formamide were purchased from Sigma-Aldrich Chemical Company.

Instrumentation. The surface morphology of substrate was measured using an atomic force microscope (Nanoscope IIIa, Digital Instruments, USA) in contact mode with a silicon cantilever (spring constant = 0.15 to 1.5 Nm⁻¹, MikroMasch, Russia).

As depicted in Figure 1, the spectroscopic RCE system used in this study is composed of (1) Xe arc lamp, (2) MgF₂ Rochon polarizer, (3) liquid in cell, (4) rotating MgF₂ compensator with known retardance, (5) MgF₂ Rochon analyzer, (6) spectrograph, and (7) multichannel detector for

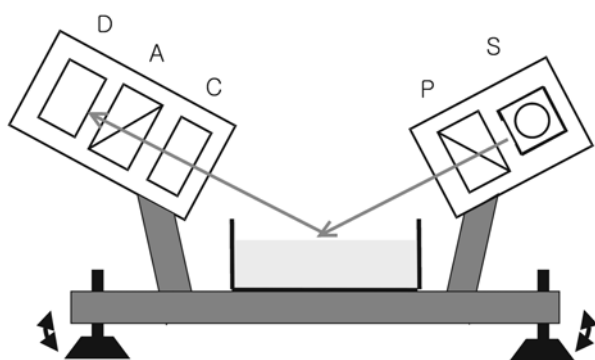


Figure 1. Schematics of rotating compensator ellipsometer used in this study. S: light source, P: polarizer, C: rotating compensator, A: analyzer, and D: multichannel detection system.

fast and spectroscopic data acquisition. This system can measure 250 nm to 820 nm range in a second. Ellipsometry measurements were performed at air-liquid interface, prism-liquid interface, and liquid-sample interface as shown in Figure 2.

Results and Discussion

The detected irradiance at each detector channel can be expressed as the azimuth of compensator, *i.e.* the product of angular velocity and time t .¹⁴

$$I(t) = I_0(1 + \alpha_2 \cos 2\omega t + \beta_2 \sin 2\omega t + \alpha_4 \cos 4\omega t + \beta_4 \sin 4\omega t) \quad (1)$$

The coefficients $\{\alpha_2, \beta_2, \alpha_4, \beta_4\}$ which carry the optical information of sample can be determined from the Fourier analysis of detected signal over the rotation of compensator. Thus the conventional ellipsometry angles $\{\Delta, \Psi\}$ are obtained from these Fourier coefficients and the azimuths of analyzer (A) and polarizer (P).

$$\Delta = \cos^{-1} \frac{\cos 2\chi \cos 2Q (1 - \cos 2\Psi \cos 2P)}{\sin 2\Psi \sin 2P}, \quad (2a)$$

$$\Psi = \frac{1}{2} \cos^{-1} \frac{\cos 2P - \cos 2Q \cos 2\chi}{1 - \cos 2Q \cos 2\chi \cos 2P}, \quad (2b)$$

where

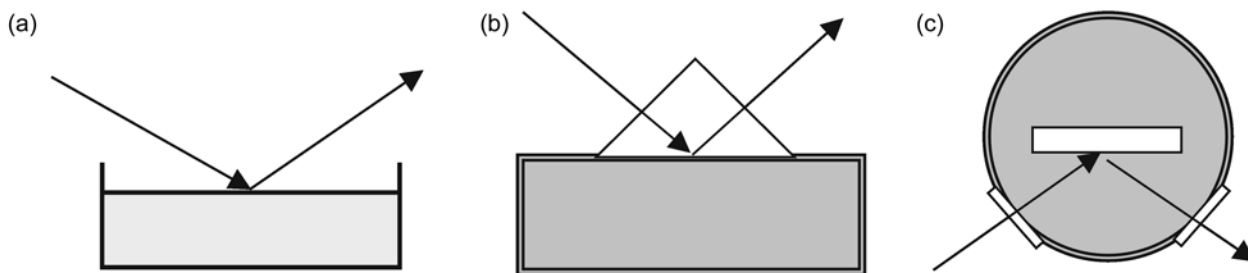


Figure 2. Configurations of measurement: (a) air-liquid interface (front view). (b) prism-liquid interface (front view). (c) liquid-sample interface (top view).

$$Q = \frac{1}{2} \tan^{-1} \left(\frac{\beta_4}{\alpha_4} \right) - A, \quad (3a)$$

$$\chi = \frac{1}{2} \tan^{-1} \left[\frac{\alpha_2 \cos 2(A + Q) \tan(\delta/2)}{2\alpha_4 \sin 2A} \right]. \quad (3b)$$

The first method we used was direct measurement of liquid surface (air-liquid interface) as shown in Figure 2a. The angle of incidence was set at 60° , close to the Brewster angle for the liquids in given spectral range. This configuration is working better with RCE than RPE or RAE, because RCE is more sensitive when Δ is close to 0° as is the case for the surface of liquid. In the second method, we used prism as an ambient as shown in Figure 2b. In these two cases, the refractive indices can be obtained directly from the measured ellipsometry angles $\{\Delta, \Psi\}$ if we have an abrupt interface between liquid and ambient. When we define the complex reflectivity ratio ρ from the Fresnel's reflection coefficient $r_{p(s)}$, for $p(s)$ wave, we have

$$\rho \equiv \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}, \quad (4a)$$

and then the refractive index of liquid, n is obtained from following relation,

$$n = n_0 \sin \theta \left[1 + \tan^2 \theta \left\{ \frac{1 - \rho}{1 + \rho} \right\} \right]^{1/2}. \quad (4b)$$

where n_0 is the refractive index of ambient and θ is the angle of incidence. When liquid is transparent or when we use only the transparent range of the measured spectrum, Sellmeier dispersion can be used to represent the optical function of liquid.

$$n^2 = A + \sum_i \frac{B_i \lambda^2}{\lambda^2 - \lambda_{0i}^2}, \quad (5)$$

where $\{A, B_i, \lambda_{0i}\}$ are free parameters to fit the measured ellipsometry spectrum.

As the third method, we measured crystalline silicon (Si) in liquid ambient. Si has been used as a substrate material for many thin film growth studies. The main benefit of using Si is its flatness of surface. As the polishing technique is well established for Si in semiconductor industry, run-to-run variation related to the surface roughness can be minimized.

Another benefit is its well-known optical properties including the native oxide intact.¹⁶ In this method, Si surface is measured in a liquid cell as shown in Figure 2c (top view). In this configuration, ellipsometer system was flipped 90° so that the Si sample could be positioned in vertical direction in liquid. The probing beam enters and exits the cell through the optical windows. As the optical properties of SiO₂ and Si are known and also the thickness of SiO₂ can be measured, the remaining optical function of liquid can be deduced from the measured { Δ , Ψ } spectra under the assumed model of 'ambient/SiO₂/Si'.

When two or more liquids are mixed together physically, we may apply the Bruggeman effective medium theory (EMT) to deduce the optical function of the mixture (17).

$$0 = f_A \frac{\varepsilon_A - \varepsilon}{\varepsilon_A + 2\varepsilon} + (1 - f_A) \frac{\varepsilon_B - \varepsilon}{\varepsilon_B + 2\varepsilon} \quad (6)$$

Here, ε_A and ε_B are the dielectric function of liquid A and liquid B, respectively. And f_A is the volume fraction of liquid A and ε is the resultant dielectric function of mixture. Dielectric function is related to the refractive index function by $\varepsilon = n^2$. This Bruggeman EMT is popular in thin film study to determine the volume fraction of ingredient or roughness thickness.^{18,19} If the substrate is microscopically rough, the material can be described as a perfect substrate separated from the perfect ambient by an effective medium layer or a roughness layer. The optical function of the roughness layer is obtained by mixing the optical function of the material and the optical function of the ambient.

Figure 3 shows { Δ , Ψ } spectra for selected liquids measured directly from its surface in air (open symbols) and those obtained from fit using Sellmeier dispersion relation (lines). Although this direct measurement is simple in use, there are some problems or limitations in this configuration: (i) there can be disturbance due to the vibration on liquid surface. It is mostly responsible for the non-zero values of in Figure 3. (ii) if liquid is highly volatile, evaporation will cause the rapid reduction of surface height. This will be a serious problem for conventional SE, because it requires tens of minutes for spectroscopic data reduction including calibration process. (iii) If conventional RPE or RAE is used, the sensitivity becomes poor for the surface of liquid as mentioned before. (iv) As the surface of liquid lies on horizontal plane always, ellipsometer should be designed in such a way that the plane of incidence lies in vertical direction. (v) Also, as the surface normal is determined by the gravity, beam alignment cannot be performed by tilt stage on sample holder. Thus, considering all these facts, conventional RPE or RAE with monochromatic detection system is not suitable for this configuration. Meanwhile, most of these problems (except (i)) could be avoided when multichannel RCE is used with configuration as shown in Figure 1.

In order to avoid these problems one can use prism as an ambient as shown in Figure 2b. However, problem (iii) still remains if RPE or RAE is used. Another problem with this

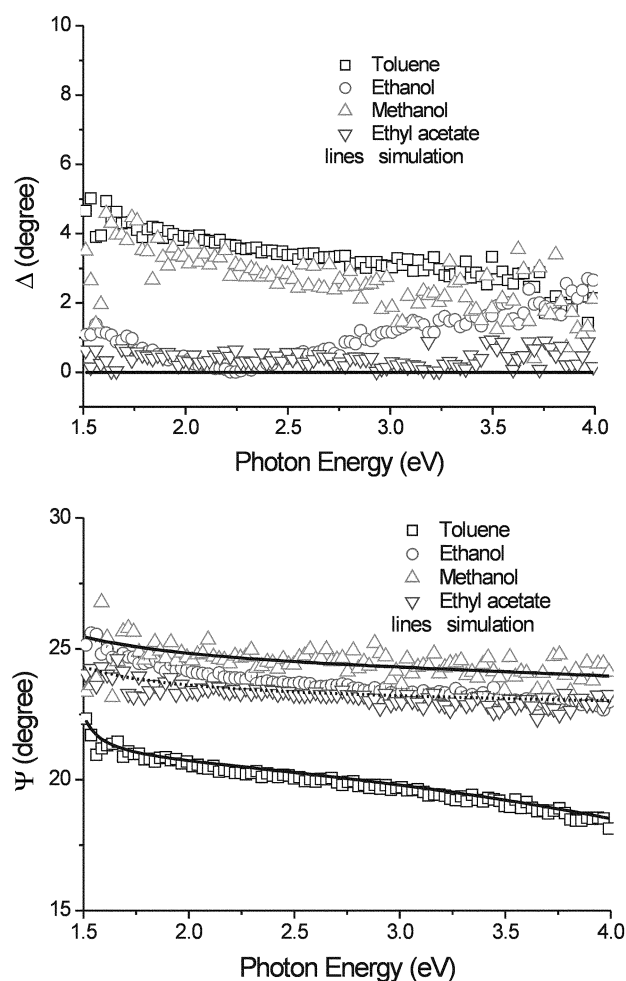


Figure 3. Symbols: { Δ , Ψ } spectra for selected liquids measured directly from its surface in air. Lines: fits using Sellmeier dispersion relation.

method arises when the index of liquid becomes close to that of prism as is the case for toluene. We had extremely poor reflection for the case. Also, in order to see other possible problem associated with this configuration, we carried out ellipsometry measurement of BK7 prism without adding liquid into the cell as shown in Figure 2b. And analysis was performed based on the optical model of 'BK7/(BK7 + Air)/air'. Here (BK7 + air) mimics the roughness of BK7 in the reflection side of surface and Bruggeman EMT was used with volume fraction of 50% in Eq. (6). Ellipsometry data were fitted by minimizing the squared difference χ^2 between the measured and calculated ellipsometric quantities of optical model.

$$\chi^2 = \frac{1}{2n - m - 1} \sum_{i=1}^n [(\Psi_{Cal}^i - \Psi_{Exp}^i)^2 + (\Delta_{Cal}^i - \Delta_{Exp}^i)^2] \quad (7)$$

Here, n is the number of points of wavelength and m is the number of floating parameters to be fitted. 'Cal' means the theoretical calculation from an assumed model, and 'Exp' means the experimentally measured data. From the analysis

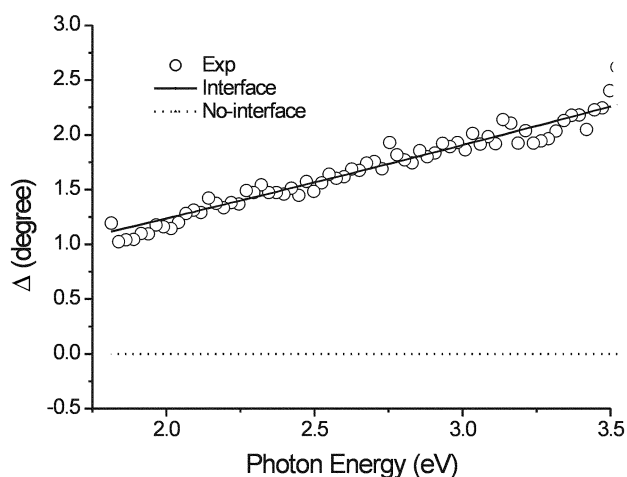


Figure 4. Δ spectrum measured from prism-ethanol interface (open symbol). Solid line: fit with roughness effect on prism surface. Broken line: fit without considering roughness.

we found the roughness of 23 nm, which indicates that there is no abrupt interface between BK7 prism and liquid. This is attributed to the imperfect polishing of prism surface and we got 13 nm of average roughness from atomic force microscope (AFM) measurement. The difference in roughness between EMT method and AFM measurement are due to the difference in the nature of sensitivity to the roughness scale.¹⁹ Therefore, after filling liquid into the cell, the optical function of liquid can be obtained from the Sellmeier expression for liquid under the assumed model of 'BK7/(50% BK7 + 50% liquid) 23 nm/liquid'. Figure 4 shows the measured spectrum from prism-ethanol interface (open circles) and fit with and without considering roughness effect (lines). We can see that better fit (solid line) can be obtained when the roughness or interface between prism and liquid is considered. In this fit process, we got average difference of 0.005 in refractive index between these two fits and less uncertainty when we considered roughness, which can be imagined from the fit. When this prism-liquid configuration is exploited, one needs to check the surface quality of the prism.

In order to avoid all problems associated with air-liquid and prism-liquid configurations, we performed measurement on liquid-Si interface as shown in Figure 2c. In this configuration, we have higher reflection compared to two former configurations as we have distinctive refractive indices for liquid and Si. Thus the optical function of liquid can be inverted from the measured $\{\Delta, \Psi\}$ spectrum such as shown in Figure 5 using the optical model of 'liquid/SiO₂(23Å)/Si'. For comparison, Figure 6 shows fitting errors of two measurements performed at air-liquid (ethanol) and liquid-Si interfaces. As we expected, the fitting quality for the spectrum measured at liquid-Si is better. With this configuration, most problems mentioned earlier can be eliminated including the surface roughness effect of prism and index-matching problem between liquid and prism.

Table 1 shows the Sellmeier parameters and resultant refractive indices for various liquids obtained from mea-

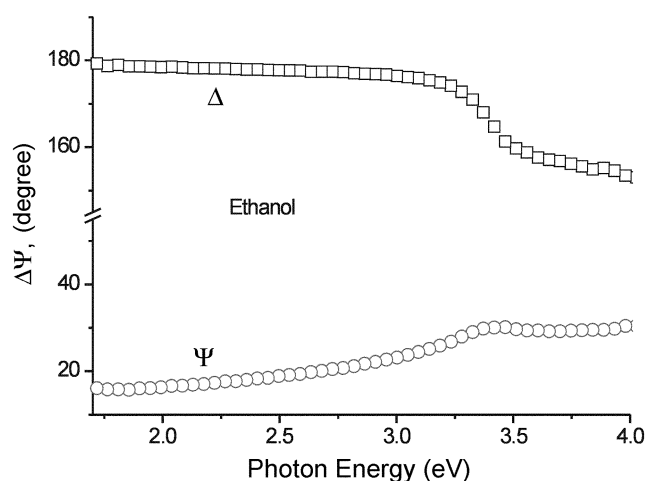


Figure 5. $\{\Delta, \Psi\}$ spectra for crystal Si measured in ethanol.

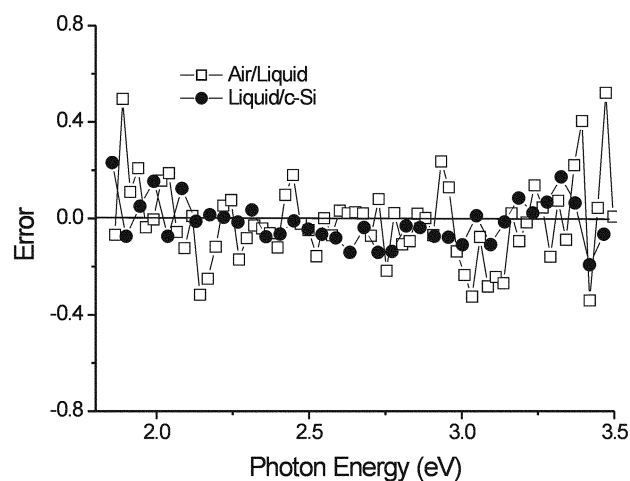


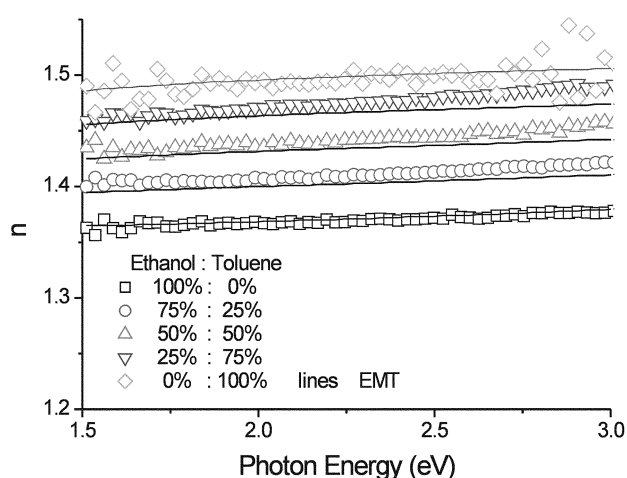
Figure 6. Fitting error of $\{\Delta, \Psi\}$ spectra measured from air-liquid interface (open square) and liquid-sample interface (filled circle).

surements from air-liquid interface along with liquid-Si interface. Spectrum range for the analysis was 1.5 to 4.0 eV (or equivalently, 310 to 825 nm) and two sets of Sellmeier terms were used. Those values in seventh column show refractive indices from the Sellmeier parameters and the last column shows those from Sigma-Aldrich Fine Chemicals. We find that spectroscopic RCE provides refractive indices of most liquids within 0.11% error.

Finally, we measured the optical function of mixture of ethanol and toluene at different volume ratio using prism-liquid interface configuration. Also we used Bruggeman EMT to deduce the optical functions of mixture at different volume fraction using Eq. (6). Figure 7 shows that the resultant optical functions obtained from two methods. They match each other within the error margin of ± 0.014 in refractive index. These error margins are comparable to those reported by Mehra who compared data from refractometer with those by Lorentz-Lorent EMT analysis for the mixture of hexadecane and heptadecane with *n*-alkanols.²⁰ As only a single wavelength data are used in this study, the validity of Lorentz-Lorent EMT can not be discussed at the

Table 1. The optical parameters for various liquids obtained from RCE. For the definitions of parameters, see Eq. (5)

Liquid	Sellmeier parameters					Sellmeier (589 nm)	Ref. 20
	A	B ₁	C ₁	B ₂	C ₂		
Toluene	0.605	0.933	143.3	0.609	136.3	1.497	1.496
Ethanol	0.782	0.525	135.0	0.472	140.2	1.355	1.363
Methanol	0.978	0.369	152.9	0.408	8.9	1.334	1.329
Methylene chloride	0.549	0.868	145.0	0.535	54.8	1.417	1.424
Chloroform	0.958	0.769	119.0	0.394	41.4	1.468	1.446
Ethyl acetate	0.542	0.923	82.9	0.413	85.9	1.380	1.372
Hexane	0.671	0.677	109.9	0.493	112.0	1.373	1.375
Tetrahydrofuran	0.415	0.647	101.0	0.830	107.4	1.393	1.407
Ether	0.461	0.507	124.2	0.742	153.4	1.337	1.353
Dimethylformamide	0.738	0.916	109.6	0.409	111.8	1.453	1.431

**Figure 7.** The optical function of mixed liquid (ethanol and toluene) at different volume ratio. Symbols: deduced from the direct measurement from prism-liquid interface of mixture. Lines: calculated from EMT with two known optical functions of pure ethanol and toluene. Fig. 1.

moment. However, it can be said that when two or more liquids are mixed together the optical properties of mixture can be obtained by EMT when the optical properties of individual liquid and its volume fraction are known. However, this EMT method can be used only when liquids can be mixed well without any chemical reaction.

Conclusion

We investigated three different measurement configurations to deduce the optical functions of liquids using rotating compensator spectroscopic ellipsometry with multi-channel detection system. Due to the high sensitivity of RCE over conventional RPE or RAE for liquid, the refractive index can be obtained from the direct measurement from air-liquid interface or prism-liquid interface. For prism-liquid interface, one needs to check the surface roughness of prism for accurate analysis. When we used our proposed configuration of liquid-Si interface, we had better sensitivity due to the high reflection and less problems associated with

environment. Finally, Bruggeman effective medium theory was introduced to deduce the optical function of mixed liquid.

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