Angle-resolved evanescent-wave cavity ring-down spectroscopy for thin film-solid interface characterization

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A new method, that involves Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS), is presented. This method is useful for the study of thin films on optical solid surfaces. The new design of experimental set-up incorporates a semicylindrical prism with a plane surface where the Total Internal Reflection (TIR) effect appears. The antireflex (AR) coated cylindrical surface of the prism induces the stability of resonant cavity. The evanescent wave generated at the plane surface of the prism probes the absorption by matter in the vicinity of the prism. A general discussion of design criteria is presented to quantify intrinsic losses, and then absorption spectra for Rhodamine chloride R590 from 555 to 560 nm are presented to demonstrate the sensitivity of the system. The layer of R590 on BK7 surfaces is deposited from a solution of R590 in ethanol (92% purity) with 51 mg/l concentration. After vaporization of the ethanol the dye layer on surfaces is supposed to be uniform. This implementation of TIR surface in a resonant cavity provides a powerful new spectroscopic tool especially to angle-resolved diagnostic for interfaces and thin-films. The loss spectrum can be obtained for an angular range from the TIR critical angle to a maximum angle when the resonance of system is lost.

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1. Introduction

The cavity ring-down spectroscopy (CRDS) until now was used extensively for gas phase studies.

The principles and applications of CRDS have been reviewed elsewhere [1]^2. To extend CRDS to condensed matter, especially for surface and thin films studies, the properties of total internal reflection (TIR) are employed.

For a plane wave incident on a perfectly smooth interface between two media with indices of refraction n_1 and n_2 (n_1>n_2), TIR occurs when the angle of incidence θ_i exceeds the critical angle, defined by:

$$\theta_c = \sin^{-1}(n_2 / n_1) \qquad (1)$$

which in theory provides a perfect broadband mirror, but in practice the reflectivity is less than unity due to surface roughness scattering and nonspecular transmission arising from the nonplanar character of real wave fronts. An electromagnetic field called the „evanescent wave” (EW) penetrates a small distance into the medium with low index and propagates parallel to the surface in the plane of incidence.

This paper describes a new method that extends CRDS, namely Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) [2], to interfaces of condensed matter involving a semicylindrical prism. The innovative cavity design uses the narrow band width restriction of conventional CRDS, high reflectance dielectric mirrors, while provides a low intrinsec cavity loss and a well-defined relationship between photon decay time and absorption. The new method could be called Angle-Resolved Evanescent-Wave Cavity Ring-Down Spectroscopy (AREW-CRDS).

The implementation of AREW-CRDS concept enables to investigate absorption/polarization/fluorescence properties of thin films correlated with the penetration depth of evanescent wave (EW) in the medium with low refractive index.

For a resonator with TIR surface inside, the cavity design that will yield maximum sensitivity arises from an interplay between the factors that optimize a conventional CRDS experiment and the factors that influence the magnitude of evanescent wave absorption.

2. Theoretical considerations

The resonator design that minimizes intrinsec loss, while providing a sufficiently long decay time to achieve maximum digitization accuracy, will be optimal for a given absorption loss. A laser pulse is injected into the cavity through a cavity mirror to experience a mean lifetime τ given by [3]:

$$\tau(\omega) = \frac{t_r}{1 - R(\omega) + L_{bulk} + L_{surf} + L_{diff} + L_{coup} + L_{nspec} + \sum_i \sigma_i(\omega) \int_0^d N_i(\xi) d\xi} \qquad (2)$$

where: t_r is the photon round-trip transit time for a cavity of L legth, σ_i and N_i are the absorption cross section and number density of species i, respectively, d is the effective sampling depth for the evanescent wave, 1-$R(\omega)$accounts for intrinsec cavity losses arising largely from the frequency-dependent mirror reflectivities when diffraction losses are negligible. The other terms from denominator are the individual round-trip losses for media inside cavity: L_{bulk} corresponds to bulk loss, L_{surf} -surface scattering loss, L_{dif} –diffraction loss, L_{coup}-coupling loss and L_{nspec}-nonspecular loss, respectively.

The individual round-trip losses, L_{bulk}, L_{surf}, L_{diff}, L_{coup}, L_{nspec} (in parts per million or ppm), are detailed in [2].

The determination of optical absorption is transformed from the conventional power-ratio measurement to a measurement of time. The effect of the intermediate layers on TIR surface is clearly relevant to the propagation of EW [3].

The presence of absorbers disturbs the EW. A general applicability to surfaces is achieved because the TIR condition is not perturbed by the presence of a film that is thin relative to the evanescent wave decay length, but sufficiently thick to achieve the chemical equivalence of a semi-infinite surface.

The penetration depth of the evanescent field is [4]:

$$\delta = \frac{\lambda_0}{4\pi n_2} \frac{1}{\sqrt{(\sin\alpha_1 / \sin\alpha_c)^2 - 1}} \tag{3}$$

where: λ_0 is the wavelength of optical radiation, α_1-angle of incidence on TIR surface in n_1 medium, α_c-the critical angle of total reflection. For typical values: λ_0=560 nm, α_1=45°, n_1=1.5168 for BK7 and n_2=1 for air, α_c=41.2° and δ=114.3 nm are obtained. Greater divergence of the laser beam reduces the penetration depth [4]. Mathematically seen the penetration depth concerns the 1/e value of the intensity of the light field at the interface, but more deeply lying layers of the sample medium can also be „seen”, if the sensitivity of detector is sufficient.

The extent of EW absorption by a film of given thickness and absorptivity is a function of the angle of incidence and the index discontinuity at the TIR surface, which determine the amplitude and the penetration depth of the evanescent field [5].

As the angle of incidence approaches the critical angle or as the index discontinuity is reduced, the effective sampling depth increases as well as an enhancement of the local electric field.

The stable modes are sustained in resonators with TIR surfaces when the angle of incidence for the central ray of beam exceeds the critical angle given by the relation (1) and the weak absorption limit in the bulk material or films are fulfilled.

A discrete set of allowed angles of incidence exists for a given index discontinuity:

- the incidence angle that is closest to the critical angle will provide maximum sampling depth and the smallest number of internal reflexions in cavity;
- when the incident angle is far from the critical angle the losses can reach a threshold when the resonances are lost.

For films that are thin relative to the EW decay length, a direct comparison to a transmission spectrum is possible.

For bulk materials or surface absorbers, a linear dependence of the effective sampling depth on wavelength results in band distorsion due to enhanced sensitivity at different wavelengths.

However, the effective sampling depth can provide an established and simple relationship between the absorption loss per pass in a resonator and the mean photon lifetime as well as a well-defined path length for quantitative spectroscopy. The distorsion effect can be evaluated by another optical method. This effect is roughly analogous to the „inner filter” effect in conventional fluorimetry in which a high concentration of fluorophore attenuates the incident light. TIR may even occur at the interface between the intermediate layer and the external low refractive index medium.

Regardless of their refractive indices, intermediate layers cannot thwart TIR at some interface in the system, if it would have occured without the intermediate layers [3].

If a metallic conductor, unmatched refractive index or unhomogeneous dielectric material are deposited onto the surface, entirely new phenomena can be observed [6, 7, 8].

For typical experimental conditions, the EW illumination is of an elliptical Gaussian profile and the polarization and the penetration depth are approximately equal to those of a plane wave.

The EW intensity for each polarization is function of incident electric field polarization. The evanescent electric field is transverse to the propagation direction only for the $\perp$ polarization. The $\parallel$polarization field cartwheels along the surface with a spatial period of $\lambda_0/(n_1\sin\theta)$ [3].

After the substraction of the baseline loss signal for cavity without thin film from the general loss signal of the system with sample film on TIR surface, the concentration of absorber molecules is calculated [9]:

$$C = \frac{\alpha}{\sigma} \quad \text{(molecules/cm}^3 \text{ or ppm)} \tag{4}$$

where: α is absorption coefficient and σ is absorption cross section of the surface-bound species for the pumping wavelength. In addition, chemically different surface sites and surface chemical reactions can occur and are likely important on the nascent glass surface of the prism.

3. Experimental

The basic configuration of the resonant cavity with 0.20 m length involved here uses CRDS mirrors with maximum reflectivity of 99.9985% at 540 nm.

These mirrors can be used over a ± 25 nm interval around the mentioned wavelength.

All mirrors have 1 m radius of curvature and 1" diameter.

For reflectivity of 0.999985 the number of round trips is about 10000, giving an effective optical pathlength of about 2.0×10^3 m, far higher than for conventional multi-pass arrangements [10].

The ability to sample such large paths with small optical system makes this approach useful in spatially resolved analysis of thin films.

The system described below is a closed path multipass absorption cell. Experimental set-up is shown in Fig. 1.

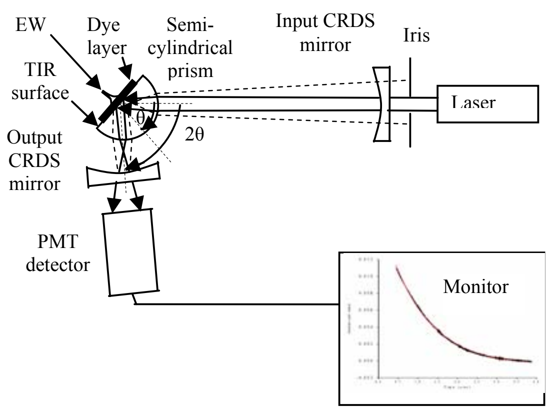

Fig. 1. Experimental set-up scheme for the EW study of thin film-solid interface.

Between mirrors, in the path of laser beam, a BK7 semicylindrical prism with 0.015 m curvature radius and 0.02 m width is inserted.

Just the semicylindrical surface of the prism was antireflex (AR) coated for visible range by ProOptica S.A.

Thus, after AR coating deposition the reflectivity decreased from 4.2% to 0.1% for the visible range.

The pumping wavelength range for ring-down cavity is 555÷564 nm, with step of 0.05 nm/s, from a ND6000 Continuum dye laser.

A Brilliant Quantel Nd:YAG laser pumps the dye laser with 532 nm radiation in order to obtain output from Rhodamine Chloride 590 (R590) dye.

The dye concentration in ethanol is adjusted to 3.7×10^{-4} (molar) in dye laser oscillator and 3×10^{-5} (molar) in dye laser amplifier.

The laser mirrors have a damage threshold of 2 J/cm^2 ≅ 532 nm for 10 ns pulsewidth.

These values can be overreached with spikes from laser output when the resonance is touched in ring-down (RD) cavity.

The output signal from resonant RD cavity is detected with a metal package H5783-20 PMT module from Hamamatsu for 300÷900 nm wavelength range.

The PMT module has 0.78 mA/W maximum cathode radiant sensitivity in 500÷650 nm range.

The CRDS signal is digitized with high speed Gage CompuScope CS12100-1M card and fit to an exponential waveform to obtain the ring-down time constant, which can be converted to a loss per cm with Los Gatos Research Inc. CRD V4.0 software.

The LGR CRD software provides a simple interface for aligning, evaluating and data logging a CRD setup.

By wrapping these algorithms in a LabView shell, LGR has also provided a flexible, modifiable and efficient starting point for customer cavity ring-down data acquisition system to specific applications.

Parameters for data acquisition are: averaging on 20 laser pulses, 5 ring-down trace acquisitions to average, sampling rate 50 MHz, voltage gauge: 100 mV/step, 1024 points/curve, 0.1 V trigger level, trigger on positive slope, 1 MΩ input impedance, parameters fit in maximum 4 iterations, negative polarity for detector, simultaneous display for signal, fit curve and difference for these traces for maximum of 100 curves in histogram.

The external trigger signal is synchronized with the ring-down event. The CRDS signal from photodetector is digitized and fed to computer, which fits the trace to a first-order exponential function to determine the decay time constant for each pulse.

This decay time is determined by two factors: the reflectivity of the mirrors and the attenuation of the laser pulse by any absorbing medium inside the cavity.

By measuring the ring-down decay rate rather than absolute intensity of the laser pulse, shot-to-shot variations in laser output can be removed from the final spectrum.

The layer of R590 on BK7 surface is deposited from a solution of R590 in ethanol (92% purity), with 51 mg/l concentration, by vaporization of the ethanol from solution on the BK7 surface.

As shown in Fig. 1, the laser beam enters the prism through the cylindrical surface of prism and strikes the plane surface in central part at chosen incidence angles on TIR surface: 42º, 43º, 44º, 45º, 50 º and 60º.

The first angle is the closest to the critical RIT angle.

For the critical angle (41.2º) the penetration depth has a singularity (rel.(3)), but in practice this angle is downward limited by the optical properties of media.

4. Results and discussion

For the determination of baseline loss signal, initial experimental measurements were carried with a prism without R590 layer. It was found that the ring-down time decreases and the intrinsic loss increases rapidly versus pumping laser power (Fig. 2(a)) and wavelength (Fig. 2(b)) respectively.

The software records the round-trip optical loss/round-trip path length in ppm/cm equivalent with an absorption coefficient.

High sensitivity absorption measurements can be anticipated in 555÷564 nm spectral region for shorter wavelengths.

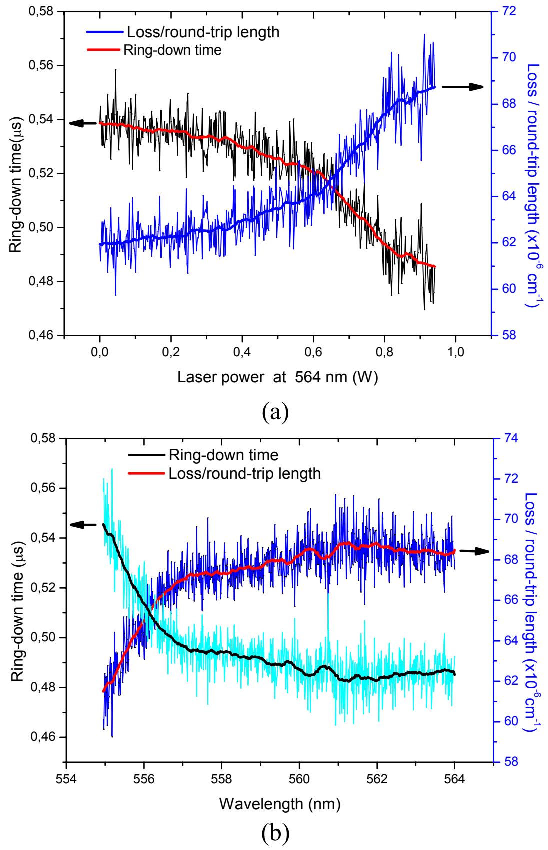

Fig. 2. Intrinsic loss/round-trip length and ring-down time for 45° incidence angle versus: (a) pumping laser power at 564 nm and; (b) wavelength of pumping radiation at 360 mW laser power.

To obtain the highest sensitivity, excitation of only the lowest order transverse cavity mode, TEM_{00}, must be employed, which significantly improves decay time precision. But, this fact is possible here just for low pumping power of RD cavity, 360 mW respectively.

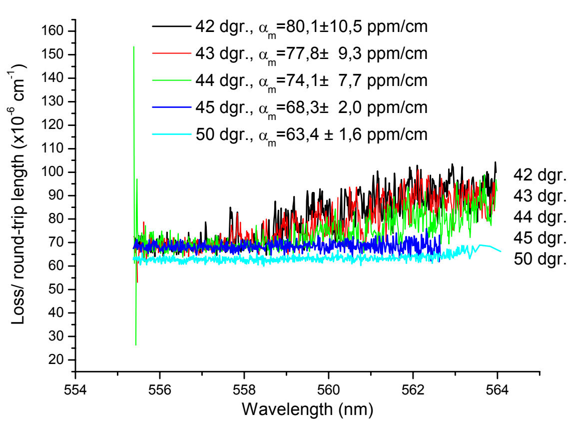

Fig. 3. Loss spectra for resonant cavity versus wavelength and incidence angle of laser beam on TIR surface at 360 mW laser power.

In Fig. 3 are shown spectra, average values and standard deviation for loss/round-trip length for different incidence angles of pumping laser radiation on plane TIR surface.

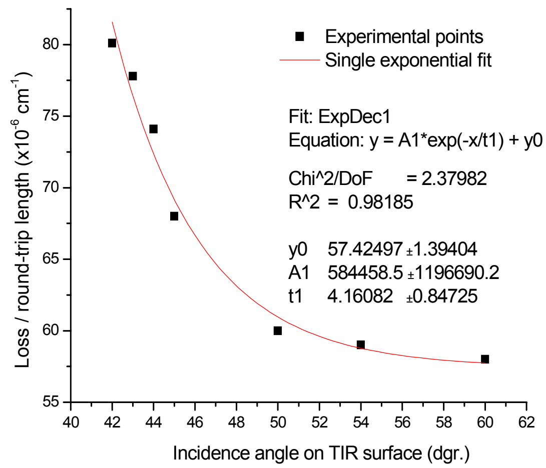

Fig. 4. Dependence of intrinsic loss versus incidence angle of laser radiation on plane TIR surface at 560 nm.

One single drop of R590 solution (51 mg/l in ethanol with 99,2% purity) was deposited on the plane surface of semicylindrical prism from Fig. 1 for the first measuremet, then other drop on incidence cylindrical surface for the second measurement. To measure the loss only for R590 dye layer on cylindrical surface, the TIR surface was wiped with ethanol.

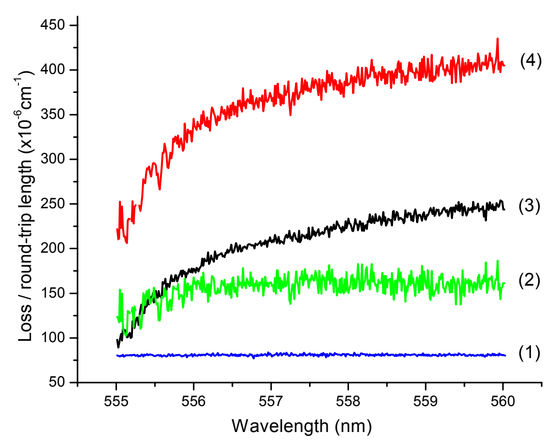

Fig. 5. Intrinsic loss (1) and loss spectra with: R590 dye on TIR surface (2), R590 on cylindrical surface (3), R590 on both surface (4), respectively, for 42° incidence angle at laser maximum power.

The extreme values corresponding to Fig. 5 for ring-down times are: 0.4903±0.0020 μs without R590 on surfaces, 0.1450±0.0028 μs with R590 on TIR surface, 0.1354±0.0005 μs with R590 on cylindrical surface, 0.0817±0.0012 μs with R590 on both surface, at 564 nm, 900 mW.

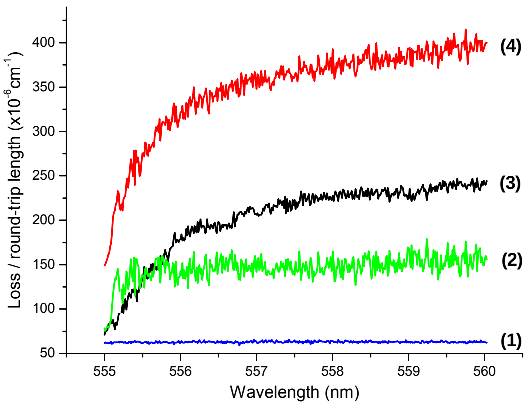

Fig. 6. Intrinsic loss (1) and loss spectra with: R590 dye on TIR surface (2), R590 on cylindrical surface (3), R590 on both surface (4), respectively, for 50º incidence angle at laser maximum power.

The extreme values corresponding to Fig.6 for ring-down times are: 0.5062±0.0022 µs without R590, 0.1802±0.0028 µs with R590 on TIR surface, 0.1406±0.0007 µs with R590 on silindrical surface, 0.0862±0.0007 µs with R590 on both both surfaces, at 564 nm, 900 mW.

The losses are found to strongly depend with wavelength for R590 layers. Most probably the spectra suggest that nonspecular transmission loss will be great relative to another sources of losses [2] for investigated spectral range. If the laser beam is narrower, then the contribution of nonspecular effects is smaller and the dependence of cavity loss versus incidence angle on TIR surface is more precise settled (Fig. 4).

The loss starts arise from 555 nm (Fig. 5-6) at scanning on 555÷560 nm range with 0.05 nm/s step, for R590 dye deposited from ethanol solution (51 mg/l) on TIR and cylindrical surfaces, because the EW-excited dye molecules adsorbed to surfaces will tend to transfer its energy to surface plasmons in the adjacent glass surface [11].

If the total loss is smaller, then the sensitivity of system is greater. To greater incidence angle than the critical TIR angle (ex. 41.2º BK7/air interface at 300K) the sensitivity of AREW-CRDS method increases.

In Table 1 are shown comparative data regarding AREW-CRDS sensitivity for two incidence angles and two wavelengths.

Tabel 1.

555 nm		560 nm	
42º	**50º**	42º	50º
Measured loss/round-trip length (x10^{-6} cm^{-1})		Measured loss/round-trip length (x10^{-6} cm^{-1})	
20.83	**15.67**	93.80	88.81

The values from Table 1 show that EW sensitivity is the best for 50º angle and 555 nm wavelength.

For the following conditions: 60º incidence angle, maximum laser power, regardless pumping wavelength, the resonances of cavity are lost (Fig. 7) for R590 layer (deposited from 51 mg/l solution) on TIR surface. This effect don't appears for smaller incidence angle.

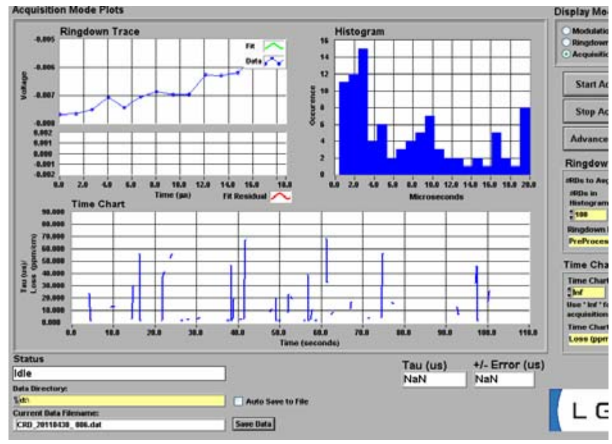

Fig. 7. The cavity resonance is lost for concentration of 51 mg/l of R590 in C_2H_5OH (99,2%) on TIR surface even at 560 nm, 60º incidence angle (LabView capture).

With the value of σ_{12}=4.17×10^{-16} cm^2 from ref. [12] and the minimum loss from Table 1, a small concentration value that could be measured with AREW-CRDS system is obtained: $C_{min.555\ nm}$=3.76×10^{10} molecules/cm^3 from rel. (4).

If the dye mass from one single drop and the area of dye layer on BK7 surface could be evaluated, then the thickness of R590 layer could be determined. The absorption spectrum for a thin film has a specific spectral feature versus a dominant thick layer [13].

The maximum sensitivity of proposed system to evaluate optical properties of the thin films on TIR surfaces is reached for the following features:

- Narrow laser beam and best collimated;
- Greatest possible incidence angle for stable resonance;
- Maximum laser power;
- Shorter wavelength in stability region for resonator;
- Curvature radius for incidence interface/diopter correlated with the distance prism-output CRD mirror, so that the cross-section of laser beam at output CRD mirror to be equal with cross-section of laser beam at input CRD mirror.

5. Conclusions

The absorption spectroscopy with EW resonant cavity has been detailed and the concepts involved here for angle-resolved EW-CRDS method were demonstrated in a proof-of-principle experiment which was carried out using a pulsed dye laser source for 555-560 nm range.

The experimental set-up proposed in this paper for the variation of beam incidence angle on TIR surface, and for the obtaining of enhanced sensitivity in EW, can evolve in an effective and reliable device for thickness monitoring of thin films, like the modern automatic spectro-ellipsometers.

The new optical method, AREW-CRDS, proposed for the optical properties evaluation of thin film on TIR surface, has shown better sensitivity for shorter visible wavelenghts and greater angles than the critical angle.

The upper limit angle is determined by intrinsec loss of resonant cavity.

The maximum sensitivity of the AREW-CRDS system is obtained in the following conditions:

- Narrow laser beam and best collimated;
- Greatest possible incidence angle for stable resonance;
- Maximum laser power;
- Shorter wavelength in stability region for resonator;
- Curvature radius for incidence interface/diopter correlated with the distance prism-output CRD mirror, so that the cross-section of laser beam at output CRD mirror to be equal with cross-section of laser beam at input CRD mirror.

It was demonstrated that AREW-CRDS technique can be applied in characterization of thin film/solid interface by the matching of resonant cavity depending of the interface particularities.

For clusters attached on a support, CRDS appears to be ideal in the study of highly diluated systems due its extreme sensitivity and because the background signal of substrate is entirely considered.

The experimental results have a important applied value for surface test procedures and also for high optical accuracy measurement techniques in thin film growth.

Once again, the monitoring of thin film growth can be performed in real time with the monolithic optics included in resonant cavity.

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