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In situ reflectance and optical constants of ion-beam sputtered SiC films in the extreme ultraviolet

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Abstract

The reflectance of freshly deposited SiC thin films has been measured in situ for the first time. SiC was deposited by means of ion beam sputtering. Reflectance was measured as a function of the incidence angle in the far and extreme ultraviolet wavelengths from 58.6 to 149.4 nm. In situ measurements allowed obtaining the intrinsic reflectance of SiC films, which is somewhat larger than what had been measured for samples exposed to the atmosphere. Reflectance measurements were used to determine the optical constants of the material in the same spectral range. We compare our data to those of the literature corresponding to SiC films deposited by different techniques and exposed to the atmosphere. In situ determined optical constants will allow a more accurate design of multilayers containing ion beam sputtered SiC layers.

OCIS Codes: 260.7200, ultraviolet, extreme; 260.7210, ultraviolet, vacuum; 230.4040, mirrors; 310.6860, thin films, optical properties; 230.4170, multilayers

1. INTRODUCTION

Mirrors with high normal-incidence reflectance at wavelengths in the far and extreme ultraviolet (FUV, λ ~100–200 nm, EUV, λ ~5–100 nm) are necessary for a wide range of applications such as space instrumentation for astronomy, synchrotron radiation devices, plasma diagnostics, free electron lasers, lithography, and spectroscopy. The development of such instrumentation has been burdened with the low reflectance of conventional coatings. Additionally, the high absorption of materials in this spectral range, particularly in the ~50-105 nm range, makes it difficult to use multilayer coatings.

For decades it has been known that Al is the material with the largest normal-incidence reflectance in the EUV and FUV above the Al plasma wavelength at ~83 nm[1]. The outstanding reflectance of Al is severely degraded after exposure to the atmosphere at wavelengths below ~200 nm. Protective coatings for Al based on MgF_2 and LiF have been successfully used to obtain a high reflectance above the cutoff wavelengths of these fluorides at 115 and 105 nm, respectively[2]. Below the LiF cutoff wavelength no transparent material able to protect Al has been found in nature, and therefore Al films are not useful as a mirror coating in the range of wavelengths shorter than ~105 nm.

Chemical-vapor-deposited (CVD) SiC is the stable material with the largest normal-incidence reflectance in the EUV down to ~67 nm, with values around or above 0.40[3]. SiC thin films deposited by different sputtering techniques have also been reported in the literature[4,5,6,7] as having good reflecting properties in the EUV, even though their normal-incidence reflectance is somewhat smaller than CVD-SiC and it moderately degrades after their exposure to the air. When compared to CVD-SiC films, sputtered SiC films offer the benefit of a low-temperature process and a lower cost; the high temperature required for CVD-SiC is not suitable for coating conventional mirrors and diffraction gratings. Furthermore, CVD-SiC grows as a rough coating, whose polishing is complicated due to the hardness of SiC.

Windt and Bach[4] proposed for the first time the use of the sputtering technique for the preparation of SiC thin films. Their ion-beam-sputtered (IBS) samples had reflectance values clearly inferior than their CVD counterparts, with reported normal-incidence reflectance ranging 0.181 – 0.217 at 92 nm as opposed to 0.427 at the same wavelength for CVD-SiC[8]. This poor performance was attributed to contamination and/or oxidation of the films during the growth process. Keski-Kuha *et al.*[5] succeeded in preparing IBS-SiC thin films with reflectance values (0.35 at 92 nm) closer to those of CVD-SiC. They provided reflectance data as a function of ageing, and showed that a degradation over time occurred mainly during the first three months of exposure to the atmosphere that amounted to 0.07 at 92 nm. Kortright and Windt[6] prepared SiC thin films by magnetron sputtering, and reported reflectance values of 0.32 at 92 nm. To determine the optical constants of the material, Kortright and Windt used reflectance measurements *vs* incidence angle that were obtained after the exposure of the samples to the atmosphere. Schwarz and Keski-Kuha[9,10] studied the degradation of IBS-SiC thin films by means of reflectance and X-ray Photoelectron Spectroscopy (XPS) measurements performed during the first hours of exposure to the atmosphere. Several approaches were considered in order to improve the stability of the films: Si enrichment of the deposited films to correct the slightly C-rich stoichiometry, ion-beam assistance to increase film density, and the use of Xe instead of Ar as a process gas. None of those attempts provided SiC films with a reduced degradation after air exposure. Larruquert and Keski-Kuha[7] determined the optical constants of IBS-SiC thin films exposed to the atmosphere for ~2 minutes. Finally, Garoli *et al.*[11] studied the dependence of the optical constants of SiC films deposited by magnetron sputtering on the C to Si atomic ratio. None of the aforementioned investigations on the reflectivity and optical constants of sputtered SiC films provided measurements performed on samples that had not been exposed to the atmosphere.

Other materials that have been proposed as reflective, single layer coatings in the EUV are B_4C[12, 13] and B[14]. These materials have a somewhat lower normal-incidence reflectance than CVD-SiC films, except for hot-pressed B_4C and IBS B_4C in the spectral region below 67 nm and 54 nm, respectively.

Recently, some multilayer coatings have been developed for EUV wavelengths longer than 50 nm [15, 16, 17, 18, 19, 20, 21, 22, 23]. Some of these novel multilayer coatings[15,16,17,18,20] involve sputtered SiC films as outer or inner layers. The design of multilayers requires the availability of accurate optical constants of the involved materials. Hence, in order to have more accurate optical constants of SiC films it is required to characterize them before they are exposed to the atmosphere.

In this paper we report for the first time to our knowledge on the reflectance of freshly deposited IBS-SiC thin films that was measured *in situ*, i.e. with samples maintained in ultra-high vacuum (UHV) conditions during the entire preparation and measurement process. Reflectance measurements, performed as a function of the incidence angle, were used to determine the optical constants of films. Section 2 describes in detail the experimental setup and procedures. Reflectance data and optical constants are provided in Section 3.

2. EXPERIMENTAL TECHNIQUES

SiC samples were prepared by IBS, i.e, by impinging energetic ions at 45° on a target placed facing the substrate. A 96.5-mm diameter, 99.9995% purity CVD SiC target was used. The target was placed in a rotatable target holder that hosts up to 4 targets that are cooled down with water. Ions were produced by means of a 3-cm hollow cathode ion gun working with a hollow cathode neutralizer; this gun and neutralizer contain no filament, which minimizes contamination. Typical deposition conditions were an ion energy of 1100 eV and a total ion current of 45 mA. Ar was used as a process gas. Thin films were deposited at a rate of ~0.09 nm/s on float glass substrates that had been later polished. The target-to-substrate distance was 15 cm. The substrate was not intentionally heated or cooled.

The sputtering deposition system is placed in a UHV chamber pumped with a turbomolecular pump. The sputtering chamber is connected in vacuum to a UHV evaporation deposition chamber and to a UHV EUV-FUV reflectometer. The reflectometer-deposition system has been described in detail elsewhere[24,25].

The base pressures were 7×10^{-8} Pa in the sputtering chamber, and 10^{-8} Pa in the evaporation and reflectometer chambers. During sputtering deposition, Ar was made to flow into the chamber reaching a total pressure of 7×10^{-2} Pa.

3. RESULTS AND DISCUSSION

The reflectance of SiC films was measured in situ, i.e., before exposing them to atmosphere. Fig. 1 displays the near-normal reflectance of a 38-nm thick SiC film measured 5° away from the normal. This is the first time that the reflectance of unexposed IBS SiC films is reported. The reflectance of CVD-SiC [5] is also displayed for comparison. CVD-SiC reflectance is somewhat larger than for the present samples prepared by IBS, except at two narrow bands in which they are coincident. Literature data on the reflectance of a 34-nm thick IBS SiC film that had been exposed to atmosphere[7] is also displayed in Fig. 1; there is a significant reflectance difference between in situ and ex situ samples, and the difference is attributed to the slight oxidation at the first contact of the films to atmosphere.

The reflectance was measured at several angles of incidence and at two perpendicular planes of incidence in order to calculate the optical constants of unexposed IBS SiC films. Fig. 2 displays the reflectance of a 38-nm thick SiC film measured at 5°, 25°, 45°, 65°, 75° and 80° from the normal. The data are an average of measurements performed in two perpendicular planes of incidence; the reason for this average is explained in the following. Radiation emerging from the monochromator onto the sample is partially polarized. The influence of polarization on reflectance can be described by a single parameter to which we shall refer as the degree of polarization *p*:

$$p = \frac{I_p - I_s}{I_p + I_s}, \qquad (1)$$

where *Ip* and *Is* indicate the fractions of the incident intensity with the electric vector parallel and perpendicular, respectively, to the plane of incidence. With this notation, the reflectance of the vacuum/thin film/substrate structure at angle θ for a certain degree of polarization is given by:

$$R(\theta)=\frac{1+p}{2}R_p(\theta)+\frac{1-p}{2}R_s(\theta), \quad (2)$$

where $Rp(\theta)$ and $Rs(\theta)$ are the reflectance for p and s polarization, respectively. When we measure reflectance in two perpendicular planes of incidence, let us say $R_1(\theta)$ and $R_2(\theta)$, p takes opposite values in the two planes, so that the average of $R_1(\theta)$ and $R_2(\theta)$ equals the average of $R_s(\theta)$ and $R_p(\theta)$, which according to Eq. (2) equals the reflectance when incoming radiation is non-polarized, i.e., p=0. Summarizing, the average reflectance over the two planes represents the reflectance that would be measured for non-polarized incoming radiation.

The search for the optical constants of films was made through the minimization of the following merit function, which involves all the reflectance measurements at a given wavelength:

$$s_j^{\ 2} = \sum_{i=1,m}\left\{R^{exp}_{\theta(i)} - R^{cal}\left[\theta(i), n_j, k_j, p\right]\right\}^2, \quad (3)$$

where $R^{exp}_{\theta(i)}$ is the reflectance measured at angle of incidence $\theta(i)$ and $R^{cal}\left[\theta(i), n_j, k_j, p\right]$ is the calculated reflectance for the trial set n_j, k_j of optical constants in the j–th iteration. Calculations involve the structure of vacuum/thin film/opaque substrate; for these calculations we used the optical constants of glass that had been previously calculated from reflectance measurements versus the angle of incidence on the bare glass substrates. In Eq. 3, i numbers the angles of incidence from 1 (5°) to m=6 (80°). In the calculation, the effect of roughness on reflectance was neglected. Fig. 3 shows the calculated optical constants of IBS SiC films. The optical constants calculated from IBS SiC films shortly exposed to the atmosphere[7] are also shown for comparison. As with reflectance, these are the first EUV optical constant data of SiC films obtained from nonexposed films. The fact that the optical constants calculated using ex situ measurements differ from those coming from in situ measurements can be understood in the sense that the former ones are not intrinsic to SiC, but effective data corresponding to the SiC film with an ultrathin surface oxide layer. Therefore, the present ones are considered as intrinsic optical constants of SiC and a multilayer involving this material must be more accurately designed with the present data. When SiC is the outermost layer of the multilayer, an additional modelling of the oxide overlayer would be required.

Fig. 4 displays the near-normal reflectance of a 64-nm thick SiC film. Data correspond to measurements performed in situ, after a short exposure to the atmosphere, and after a prolonged exposure during storage in a desiccator. Reflectance displays a noticeable drop when shortly exposed to the atmosphere, whereas this drop sharply slows down over time; the reflectance after a period of 40 days in a desiccator is expected to approach its lowest values, with no significant further decay.

4. CONCLUSIONS

The in situ EUV reflectance of freshly-deposited IBS SiC films was measured for the first time. SiC is known to slightly oxidize after contact to atmosphere, with a moderate reflectance decrease which slows down over time; therefore, the present data correspond to the intrinsic reflectance of SiC films. The reflectance measurements versus the angle of incidence were used to calculate the optical constants n, k of SiC. These optical constants are expected to be more accurate for their use to design multilayer coatings for the EUV than the previously reported ones, which had been calculated from reflectance measurements over samples shortly exposed to the atmosphere.

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FIGURE CAPTIONS

Fig. 1. (color online) Reflectance *vs* wavelength of an IBS SiC film measured in situ. The reflectance reported in the literature for IBS coatings shortly exposed to the atmosphere (Ref. 7) and of CVD SiC coatings (Ref. 5) are also shown for comparison.

Fig. 2. (color online) Reflectance *vs* wavelength of an IBS SiC film for various angles of incidence measured away from the normal to the sample. Reflectance corresponds to nonpolarized radiation.

Fig. 3. (color online) The optical constants of IBS SiC films *vs* wavelength obtained for freshly deposited films measured in situ. The data obtained for samples that had been shortly exposed to the atmosphere (Ref. 7) are also shown for comparison.

Fig. 4. (color online) In situ reflectance *vs* wavelength of an IBS SiC film and the decay of reflectance for this same film after a 15-min exposure to the atmosphere and after a 40-day storage in a desiccator.

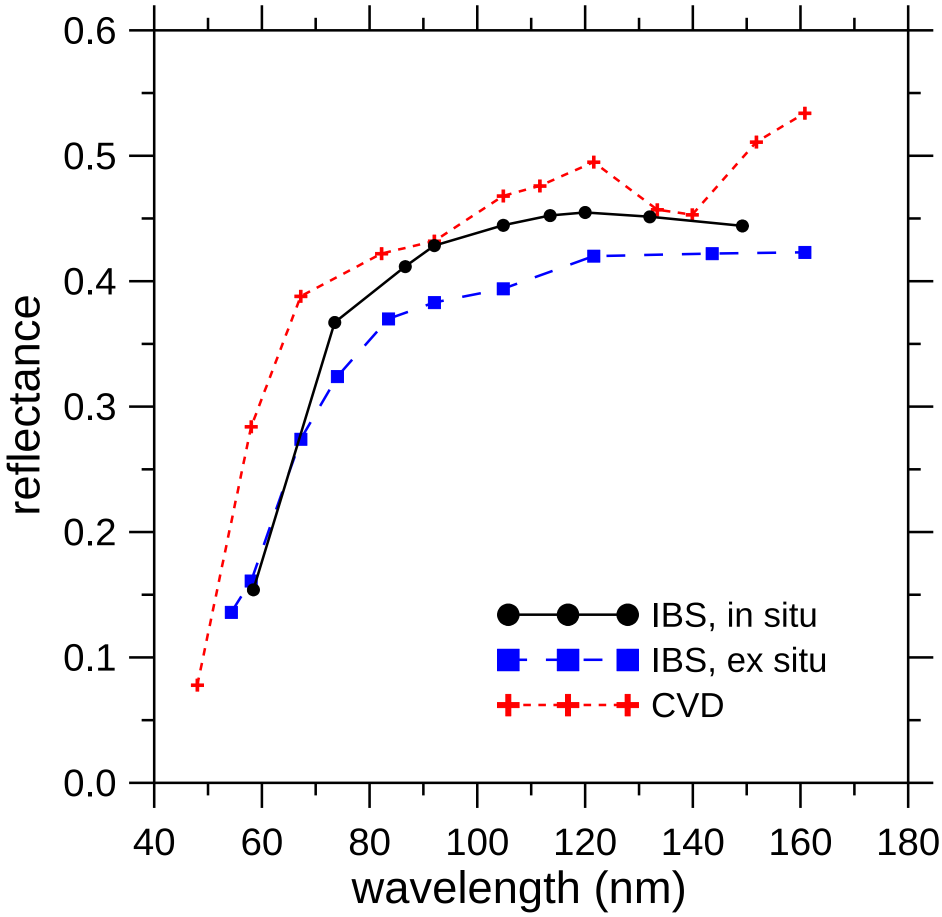
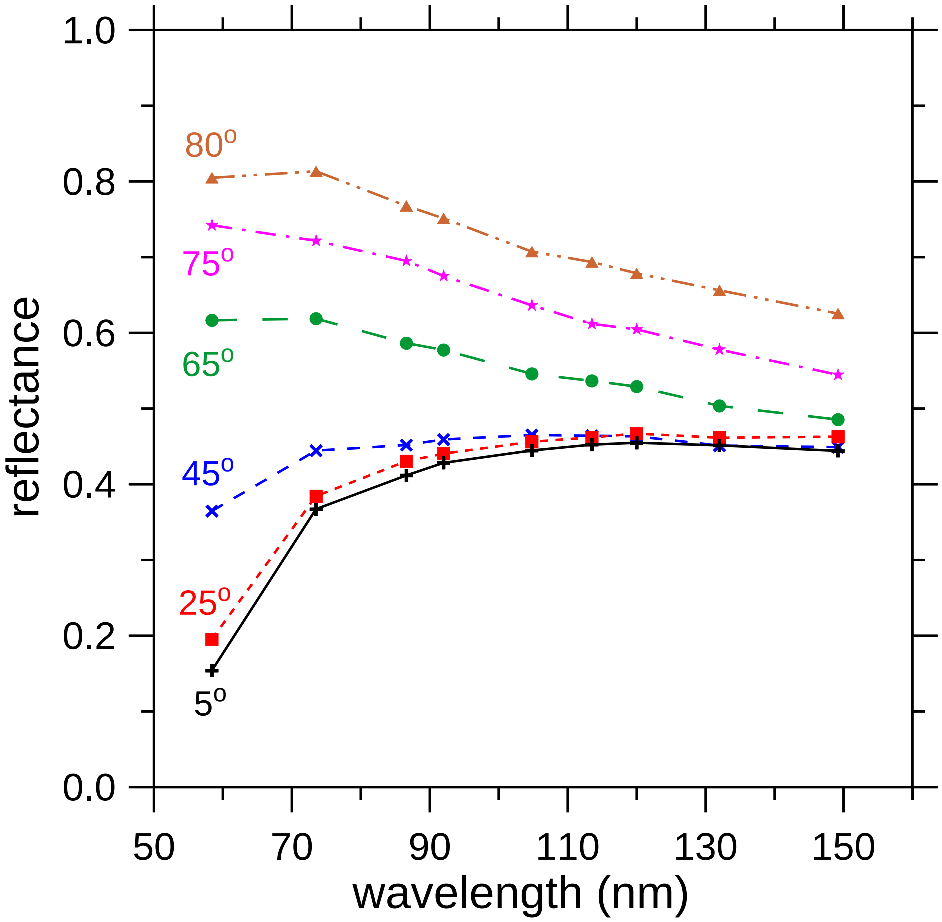

0.6
0.5
0.4
0.3
0.2
0.1
0.0
reflectance
40
60
80
100
120
140
160
180
wavelength (nm)
IBS, in situ
IBS, ex situ
CVD

Fig. 1


1.0
0.8
0.6
0.4
0.2
0.0
reflectance
50
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90
110
130
150
wavelength (nm)
80°
75°
65°
45°
25°
5°

Fig. 2

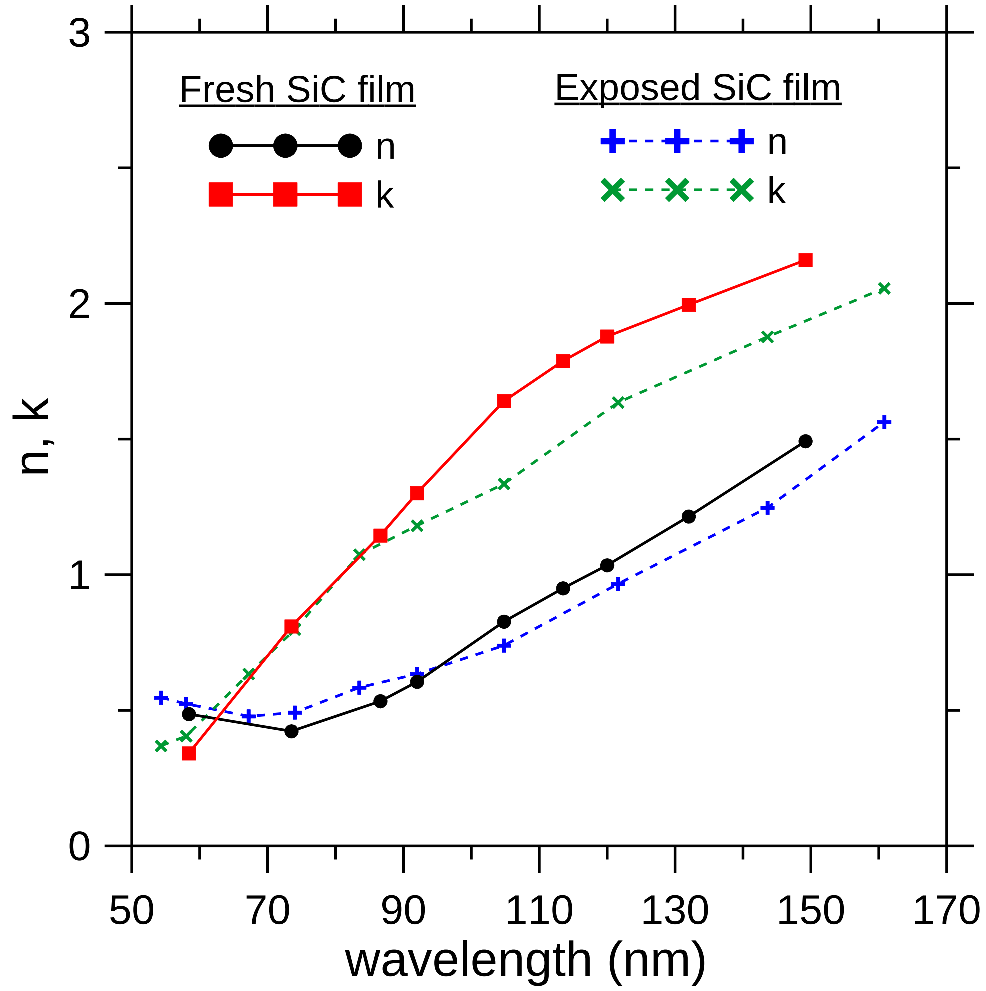
Fresh SiC film
n
k
Exposed SiC film
n
k
n, k
0
1
2
3
50
70
90
110
130
150
170
wavelength (nm)

Fig. 3

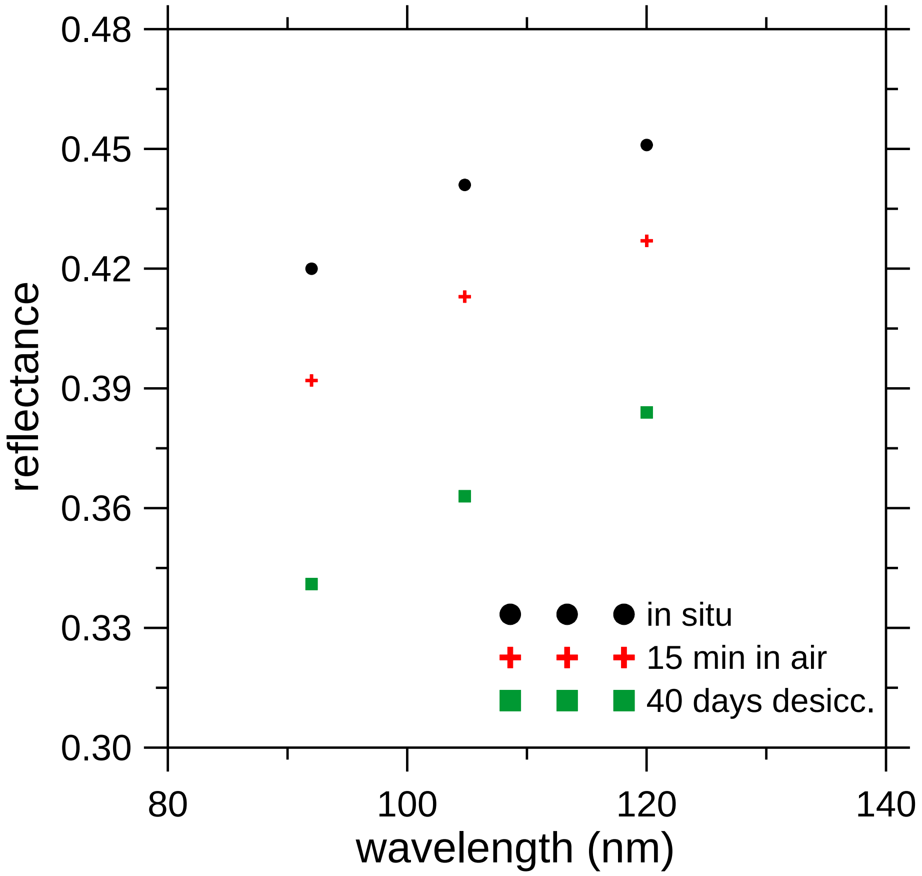
0.48
0.45
0.42
0.39
0.36
0.33
0.30
reflectance
80
100
120
140
wavelength (nm)
in situ
15 min in air
40 days desicc.

Fig. 4