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Reflective coating for near infrared immersion gratings

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ABSTRACT

Achieving high reflectivity from an immersed grating facet can be challenging in the near infrared. The reflectivity of metallic coatings in common use, such as Al and Cr/Au, decrease with decreasing wavelength in the near IR. A layer of copper on ZnSe or ZnS should have a high, immersed reflectivity based on tabulated values of refractive index, but in fact performs poorly. We attribute this to a chemical reaction between the copper and the selenium or sulfur.

A non-reactive intermediate layer can prevent this problem. Since reflectivity at an interface increases with increasing difference in refractive index, it is beneficial to choose an intermediate layer of low index. A further improvement is gained by adjusting the layer thickness so that reflections from the two interfaces of the intermediate layer add constructively.

We sputtered 130 nm of SiO_2 onto ZnSe and ZnS substrates followed by 200 nm of Cu. The copper was then coated with 5 nm of SiC as a protective capping layer. Immersed reflectivity measured shortly after coating exceeded 95% between 1500 and 1100 nm and exceeded 90% down to 850 nm. A repeat measurement after long term exposure to high humidity conditions showed no changes.

Keywords: immersion grating, near infrared, metal coating, reflective coating, ZnSe, ZnS

1. INTRODUCTION

The immersion grating is an enabling technology for increasing the resolution of a spectrograph without increasing its physical size. High quality immersion gratings have been demonstrated in silicon[1] and germanium[2] for use in the infrared. There is a need to produce immersion gratings for the near infrared and even the visible. Since the benefits of immersion scale with refractive index, efforts on near infrared immersion gratings have focused on zinc selenide (ZnSe) and zinc sulfide (ZnS). These have the highest index and lowest optical absorption of near infrared transmitting materials that are readily available[3]. Both are produced in relatively large sizes (up to 2.5 inch thick) with good optical quality.

While fabrication difficulties increase at shorter wavelengths, it is also a challenge to achieve high reflectivity in immersion from the gratings facets. Since the Fresnel reflectivity of ZnSe-air interface is only 18%, a reflective coating must be applied. For high diffraction efficiency one would like a facet reflectivity of at least 90% (see WINERED spectrograph requirements[4]).

We focused our efforts on metallic coatings because of their successful use on immersion gratings at longer wavelengths. Jaffe's group at the University of Texas used an aluminum coating with good results on silicon immersion gratings for the 1.1 to 5.5 μm range[1]. At LLNL a Cr/Au reflective layer performed well on silicon gratings in the 3 to 5 μm range[5] and on germanium gratings for 8 to 13 μm operation[2]. Metallic coatings offer broadband reflectivity, high tolerance to thickness variations, and can be much thinner than a dielectric coating of equivalent performance.

Section 2 presents experimental results on single layer metallic coatings on ZnSe and ZnS and the discrepancy between

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calculated and observed reflectivity. Section 3 discusses the nature of these problems and the modeling of a possible solution. In section 4 experimental data is presented that demonstrates the solution. Section 5 gives results on long term environmental stability of this coating. Section 6 presents conclusions and future work.

2. IMMERSED REFLECTIVITY OF SINGLE LAYER METALLIC COATINGS FOR ZNSE AND ZNS

A previous paper[6] reviewed the literature of metallic coatings on ZnSe and found little other than adhesion data for electrical contacts. In that work we also considered several metals known to have high reflectivity in the near infrared as possible candidates: aluminum, gold, copper and silver.

Gold is chemically very inert, which is good for resistance to the environment, but gives it very poor adhesion without a thin underlying layer of a reactive metal such as chromium or titanium. Although Cr/Au performs well in the mid and long wave infrared, the absorption of chromium increases at shorter wavelengths. To maintain an immersed reflectivity of 90% at 0.9 μm, calculations show that the Cr thickness must be less than 1.2 nm, not a practical consideration.

Aluminum is a very common and easily deposited coating material. Bare aluminum is protected from the environment by several nm of oxide. We sputtered 100 nm of aluminum onto a 25.4 mm diameter polished ZnSe window and measured the reflectivity in immersion. Figure 1 compares the measured reflectivity with that calculated from the optical constants[7] of Al and ZnSe. The agreement is quite good. Unfortunately aluminum has a dip in reflectivity centered at 850 nm due to interband transitions. The wings of this dip reduce the reflectivity out to about 1.2 μm. As a result the immersed reflectivity of the aluminum coating does not meet the 90% requirement below 1.1 μm. One must search further for a satisfactory coating for a near infrared immersion grating.

Copper is known to react at room temperature with the selenium[8] in ZnSe to form copper selenide. A chemical bond normally results in good adhesion. This has been observed experimentally. One would expect similar chemical bonding with the sulfur in ZnS. Our assumption was that the selenides or sulfides should have little absorption in the few nm thick layers that might be formed.

An older model Balzers magnetron sputtering system was available for our experiments. It uses a cryopump to produce vacuum and had slight modifications to the substrate platform. The sputtering chamber was already set up with copper targets and we coated 25.4 mm diameter polished windows of ZnSe and ZnS in separate runs. Coating thicknesses of 153 nm were measured on the ZnSe and 148 nm on the ZnS.

We measured the spectral reflectivity using a double path monochrometer. The results were unexpected. As seen in figure 2 the measured immersed reflectivity tracked the calculated values down to 1.2 μm then dropped sharply, below 85% at 1 μm. To help understand the discrepancy the front surface reflectivity of the copper was also measured (see figure 3) again there were large deviations from the theoretical values.

3. RESOLUTION OF THE DISCREPANCY AND POSSIBLE SOLUTIONS

Visual inspection showed no detectable discoloration on any of the coatings. However copper is a reactive metal. Our working assumption was that the front surface of the copper was oxidized either through atmospheric exposure or possibly from the presence of residual oxygen in the sputtering chamber due to a small air leak. The problem of most concern was at the immersed surface of the copper as that was the reflectivity that was relevant to immersion gratings. Since the front and back reflectivity had different spectral characteristics, the absorption mechanisms must differ. We believed that the reflection loss was due to a copper sulfide or selenide layer at the back surface. If a chemical reaction between copper and the grating substrate was the problem, then a barrier layer might be the solution.

Tantalum is used in the semiconductor industry as a barrier layer to prevent diffusion of copper metallization into silicon dioxide and silicon[9]. It was suggested[10] that it might function as a barrier between Cu and ZnSe or ZnS preventing any chemical reaction at the interface. This of course adds another material to the reflectivity calculation. Modeling showed that immersed reflectivity exceeds 90% at $\lambda = 1.3\ \mu m$ and exceeds 88% at 0.9 μm if the Ta thickness is kept to 4 nm or less. This nearly meets requirements, but perhaps there is a better approach.

From an optical standpoint, there is no reason that the barrier layer must be a metal. It could be a dielectric as long as it has low absorption over the wavelength range and is nonreactive with copper, zinc selenide or zinc sulfide. This opens up a variety of materials that are easily deposited and in common use. A dielectric layer adds two more parameters that can be used to optimize immersed reflectivity, the refractive index of the layer and its thickness.

Consider figure 4, which shows the path of rays incident on the immersed mirror. Note that the copper is now immersed in the barrier layer instead of the ZnSe. It can be seen from the equation for normal incidence reflectivity

$$R = ((n_1 - n_2)/(n_1 + n_2))^\wedge 2 \qquad (1)$$

that the reflectivity is greatest when the difference in refractive index is greatest, hence immersed reflectivity is greatest when the index of the immersing media is low. This argues for choosing a low index barrier like SiO_2 (n=1.45 at 1 μm). There is also a reflection at the interface between the ZnSe and the barrier. A low index barrier layer increases this reflectivity as well. A final step is to adjust the thickness of the barrier layer so that the reflections from both interfaces add constructively. A plot of the 3-layer reflectivity shown in figure 5 predicts that immersed reflectivity of over 90% can be achieved and that the sensitivity to barrier layer thickness is not very critical.

4. IMMERSED REFLECTIVITY OF TWO LAYER COATING FOR ZNSE AND ZNS

Having a promising coating design in hand, the next step was to coat some samples to verify that the predicted reflectivity could be achieved. At this time a more sophisticated and more tightly controlled coating system was available. The Mag 1 magnetron sputtering system shown in figures 6 and 7 was built at LLNL to deposit thin uniform layers for multilayer EUV coatings[11]. Its main function is to coat reflective optics for EUV lithography systems[12]. The chamber is designed to coat substrates up to 8 inches in diameter. The Mag-1 can deposit layers ranging from a monolayer up to 2 μm in thickness with a uniformity of 2 monolayers. Two substrate holders are held in platen, which rotates over the sputter targets to achieve the extremely good thickness uniformity. Each holder is individually spun during deposition for azimuthal symmetry (see figure 8). The base pressure of the chamber is $< 5\times10^{-7}$ torr. Ultrahigh purity argon is used as the background gas during sputtering and is maintained at a constant pressure of approximately 0.8 mtorr.

To achieve high precision the sputter rates must be calibrated. We coated witness samples prior to coating the real parts and measured the coating thickness using an x-ray diffractometer. This procedure is more accurate than measuring thickness with a profilometer.

Polished one inch diameter windows as received from vendors were used as coating substrates in this experiment. We used 2 ZnSe windows, 1 ZnS window and 1 fused silica window. The windows were taken as received from vendors, wiped with isopropyl alcohol and blown dry with clean nitrogen before being loaded into Mag-1. No sputter cleaning is done in the chamber.

The coating consisted of 130 nm of SiO_2 as a barrier layer overlaid by 200 nm of copper. Since we previously had seen evidence of bare copper oxidizing in air we added a protective capping layer of silicon carbide in a thickness of 5 nm. Calculations showed that the thin SiC layer has minimal effect on reflectivity from the air side.

After the substrates were removed from the chamber several measurements were made of the reflectivity. The first test was with a 633 nm HeNe laser with a measured output power of 1.01 mW. The laser was directed onto the coated ZnS substrate at near normal incidence. When incident on the copper capped with SiC the reflected power was 0.925 mW (R~ 91.6%). When the laser was incident through the ZnS substrate (i.e. testing the coating in immersion) the reflected power varied from 0.89 to 0.95 mW (R varies 88% to 94%) with small changes in incidence angle. This is expected because of the interference effects in the SiO_2 layer. It is consistent with a calculated normal incidence reflectivity of 92% at 633 nm.

A second test was made at a wavelength within the desired operating range of the coating using a 1053 nm, diode-pumped Nd laser reflectometer. The system is set up to measure 45 degree incidence reflectivity using beam sampling to ratio out fluctuations in the laser power. However, we were able to make measurements at near normal incidence by normalizing the measured values to a known high reflectivity mirror (R~ 99.5%). The ZnS sample measured 93.7 % reflectivity incident from the SiC side. It measured 93.4 % reflectivity through the ZnS reflecting off the immersed copper. These single wavelength results were encouraging and greatly improved over a bare copper sample.

The definitive test was performed in January 2011 producing a spectral reflectance curve and plotting reflectivity vs. wavelength (see figure 9). These measurements were taken as before using a double pass monochrometer, using a gold mirror as an absolute reflectance standard. The incident angle to the substrates is 5 degree. .

The spectral reflectance meets the design goal of >90% from 0.9 to 1.3 μm. However, the measured values are still somewhat lower than the calculated ones below 1 μm. To help ascertain why, we measured the spectral reflectance of the back side of the sample with light incident on the copper through the 5 nm layer on SiC (see figure 10). This eliminates any influence of the ZnS, ZnSe, or the SiO_2 barrier layer. A similar decrease in spectral reflectance was observed below 1 μm. So it seems most likely that this effect is due to some type of intrinsic absorption in the copper.

5. AGING TESTS AND ENVIRONMENTAL STABILITY

Two concerns for a new coating design are its durability in its environment and changes in reflectivity due to to aging. A coating whose reflectance degrades or that begins to peel off in a few months would be of little use. The fundamental design appears sound as the copper is isolated from the sulfur and selenium by a relatively thick layer of SiO_2. Silicon carbide is a very tough impermeable material and although the capping layer is quite thin it should protect the copper from oxidation.

Some consideration must be given to the conditions in which the coatings will be used or stored. Infrared spectrometer optics commonly reside in a dewar and are held under high vacuum. In WINERED, which operates at the short wavelength end of the near infrared, only the detector array and focusing lenses are in a vacuum dewar. The grating is exposed to the ambient atmosphere with temperatures ranging from 0 to 25ºC.

Since moisture and temperature cycling can degrade coatings we performed environmental testing by exposing the samples to ambient air in the telescope dome of Koyama Astronomical Observatory at Kyoto-Sangyo University. Kyoto is very wet in late spring and summer with a large annual/daily range in temperature. During the day the relative humidity in the closed dome is held to less than 70%. It increases to about 80% (sometimes up to 95%) when the dome is opened for nighttime observation. The exposure was nearly 5 months (Apr.2011 - Aug. 2011). After that, the substrates were stored in a desiccator in the optical lab of the observatory until April 2012. The coated samples were tested again for spectral reflectivity. There were no observable changes between the initial measurements in January 2011 and those made in April 2012 (see figures 11 and 12).

6. CONCLUSIONS AND FUTURE WORK

We have developed a robust reflective coating for ZnSe and ZnS immersion gratings consisting of a 130 nm thick barrier layer of SiO_2, a 200 nm thick reflective layer of copper and a 5 nm capping layer of silicon carbide. It satisfies the 90% or greater facet reflectivity requirements for the WINERED spectrograph over the 0.9 to 1.3 μm range. If higher reflectivity is needed, then calculations show that replacing the copper layer with silver should produce about 2% improvement. It is possible that sputtered silver may not show the anomalous losses seen with copper.

The coating demonstrates excellent stability and durability in the telescope environment. In May of 2012 the coated samples were placed back into the telescope dome for continued environmental exposure. Spectral reflectivity will be measured at periodic intervals.

The modeling and experimental results presented in this paper apply to an extended flat surface (i.e. an immersed mirror). The observant reader might note that the reflectivity of an immersed grating facet could differ from that of an immersed mirror due to the presence of the adjacent (or anti-blazed) facet. Looking in immersion we have a metal (copper) grating with a thin dielectric coating of SiO_2. Only one reference has been found in the literature describing the effect of a dielectric layer on echelle grating facets[13]. Kleeman and Erxmeyer computationally modeled this configuration. They separately optimized the coating thicknesses on the blazed and anti-blazed facets and found best performance when the coating was thinner on the anti-blazed than the blazed facets. We plan to experimentally verify the optical performance by depositing the coating on a small ZnSe test grating.

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REFERENCES

[1] Marsh, J. P., Mar, D. J., and Jaffe, D. T., “Production and evaluation of silicon immersion gratings for infrared astronomy,” Applied Optics 46, 3400–3416 (2007).
[2] Kuzmenko, P. J., Davis, P. J., Little, S. L., Little, L. M. and Bixler, J. V., "High efficiency germanium immersion gratings," Proc. SPIE 6273, 62733T (2006).
[3] Ikeda, Y., Kobayashi, N., Kondo, S., Yasui, C., Kuzmenko, P. J., Tokoro, H. and Terada, H., “Zinc sulfide and zinc selenide immersion gratings for astronomical high-resolution spectroscopy: evaluation of internal attenuation of bulk materials in the short near-infrared region,” Optical Engineering 48, 084001 (2009).
[4] Ikeda, Y., unpublished
[5] Kuzmenko, P. J., Ciarlo D. R.and C. G. Stevens, "Fabrication and testing of a silicon immersion grating for infrared spectroscopy," Proc. SPIE 2266, 566-577 (1994).
[6] Ikeda, Y., Kobayshi, N., Kuzmenko, P, J., Little, S. L., Yasui, C., Kondo, S., Mito, H., Nakanishi, K. and Saragaku, Y., “Fabrication and current optical performance of a large diamond-machined ZnSe immersion grating,” Proc. SPIE 7739 77394G (2010).
[7] Palik, E. D., [Handbook of Optical Constants of Solids], Academic Press, Orlando, (1985)
[8] Ouchu, A., Bastl, Z., Bohacek, J., Orita, H., Miyazaki, K., Miyashita, S., Bezdicka, P., and Pola, J., “Room-temperature reaction between laser chemical vapor deposited selenium and some metals,” Chemistry of Materials 16, 3439–3445 (2004).
[9] Wolf, S. and Tauner, R. N., [Silicon Processing for the VLSI Era Volume 1: Process Technology], Lattice Press, Sunset Beach California, 781-783 (2000).
[10] Davis, P. J., LLNL, private communication.
[11] Mirkarimi, P. B., “Stress, reflectance, and temporal stability of sputter-deposited Mo/Si and Mo/Be multilayer films for extreme ultraviolet lithography,” Optical Engineering 38, 1246-1259 (1999).
[12] Montcalm, C., Grabner, R. F., Hudyma, R. M., Schmidt, M. A., Spiller, E., Walton, C. G., Wedowski, M. and Folta, J. A., “Atomic-precision multilayer coating of the first set of optics for an extreme-ultraviolet lithography prototype system,” Applied Optics 41, 3262-3269 (2002).
[13] Kleemann, B. H. and Erxmeyer, J., “Independent electromagnetic optimization of the two coating thicknesses of a dielectric layer on the facets of an echelle grating in a Littrow mount,” Journal of Modern Optics 51, 2093-2110 (2004).

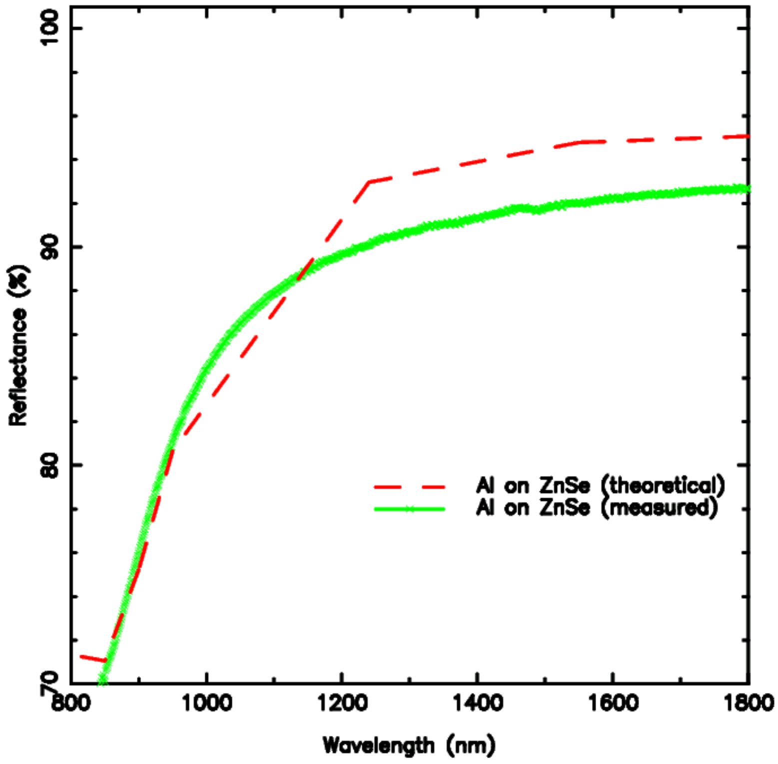

Figure 1. Comparison of calculated and measured spectral reflectance of a sputtered aluminum coating immersed in ZnSe

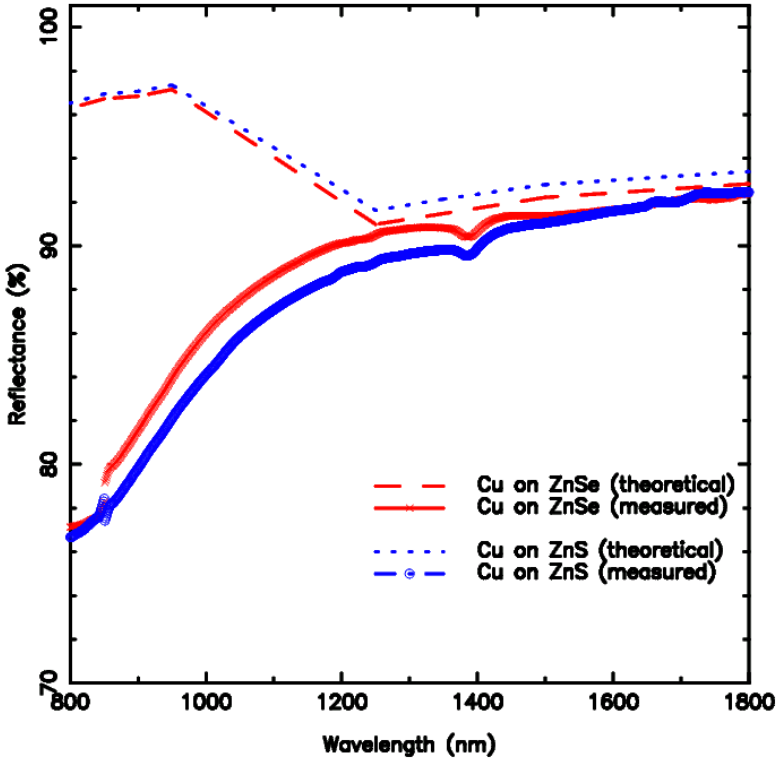

Figure 2. Comparison of calculated and measured spectral reflectance of a sputtered copper coating immersed in ZnS and ZnSe

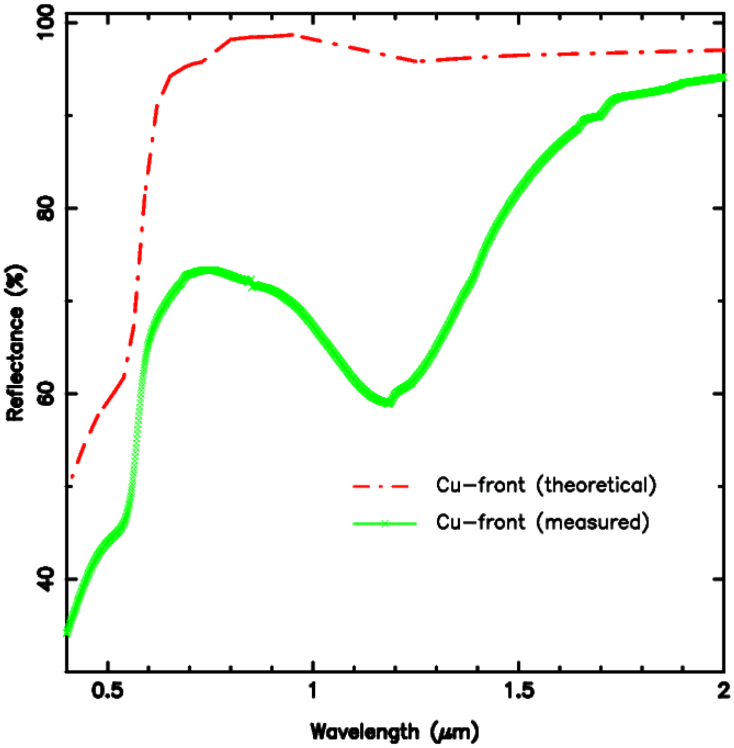

Figure 3. Comparison of calculated and measured spectral reflectance of a sputtered bare copper coating in air

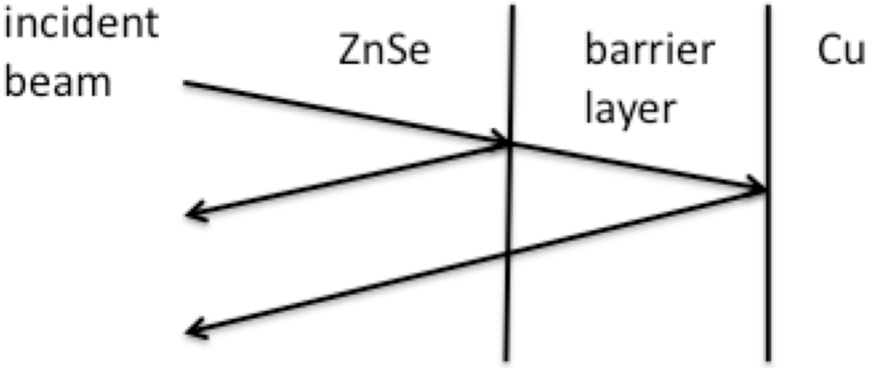

Figure 4. Light incident on an immersed metal mirror with a barrier layer produces reflections from 2 interfaces

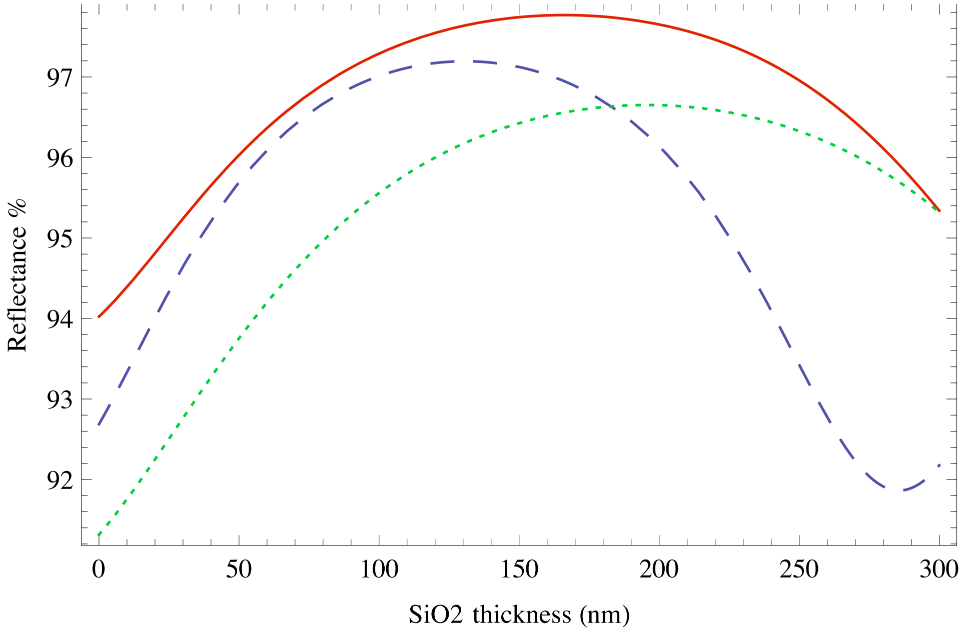

Figure 5. Calculated effect of SiO2 barrier layer thickness on normal incidence reflectivity of a Cu mirror immersed in ZnSe at several wavelengths (dashed blue line 0.9 µm, solid red line 1.1 µm, dotted green line 1.3 µm)

Figure 6. The Mag-1 magnetron sputtering system was used to deposit the SiO_2-Cu-SiC coatings on ZnSe and ZnS discs

Figure 7. Two sputter targets inside the Mag 1 chamber

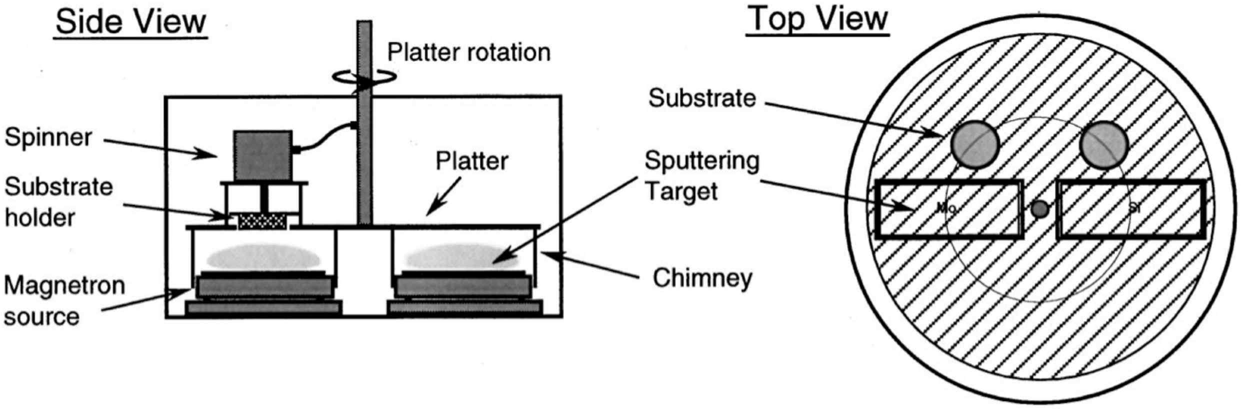

Figure 8. Schematic drawing of the Mag-1 sputtering system

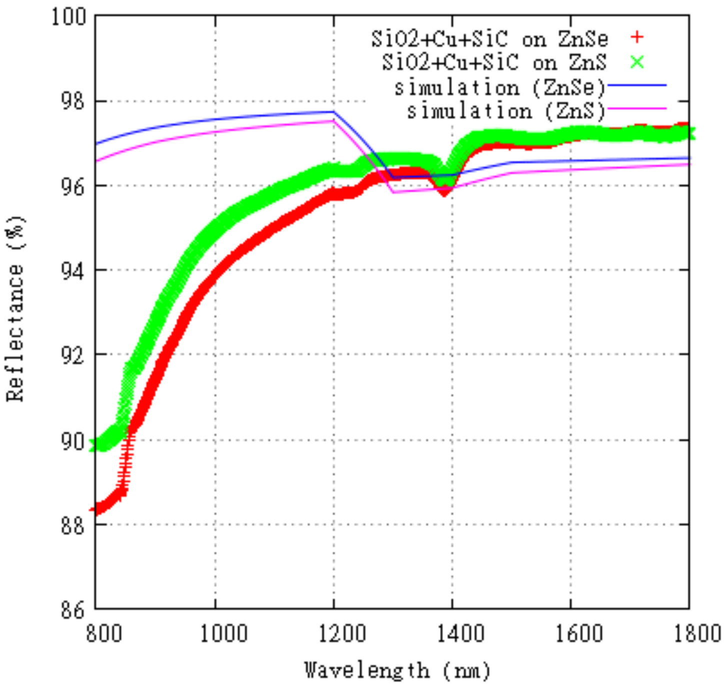

Figure 9. Measured (1/11) and calculated spectral reflectance of SiO_2-Cu-SiC coating on ZnS and ZnSe substrates. Values are for immersed reflectance with light incident through the ZnS or ZnSe substrate.

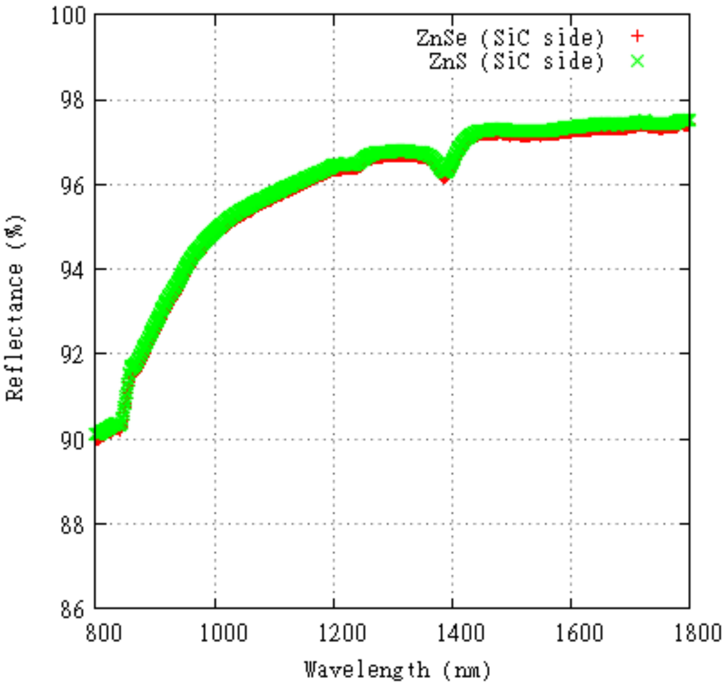

Figure 10. Measured (1/11) spectral reflectance of SiO_2-Cu-SiC coating on ZnS and ZnSe substrates. Reflectance values are with light incident through the 5 nm SiC capping layer. Comparison with figure 9 shows that excess absorption relative to calculated value is intrinsic to the copper.

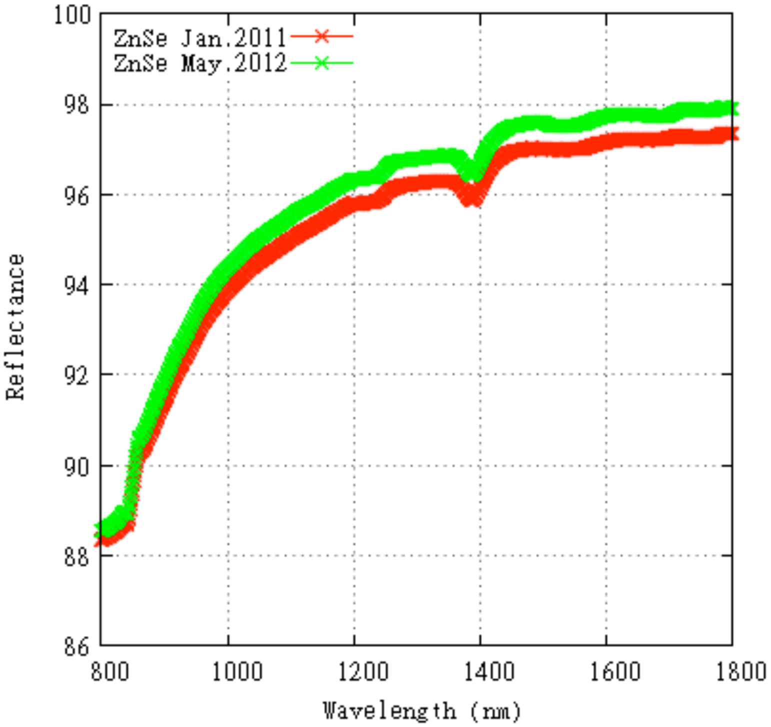

Figure 11. Comparison of immersed spectral reflectivity of SiO_2-Cu-SiC coating on a ZnSe substrate before and after long term exposure to a humid environment. No significant change is noted.

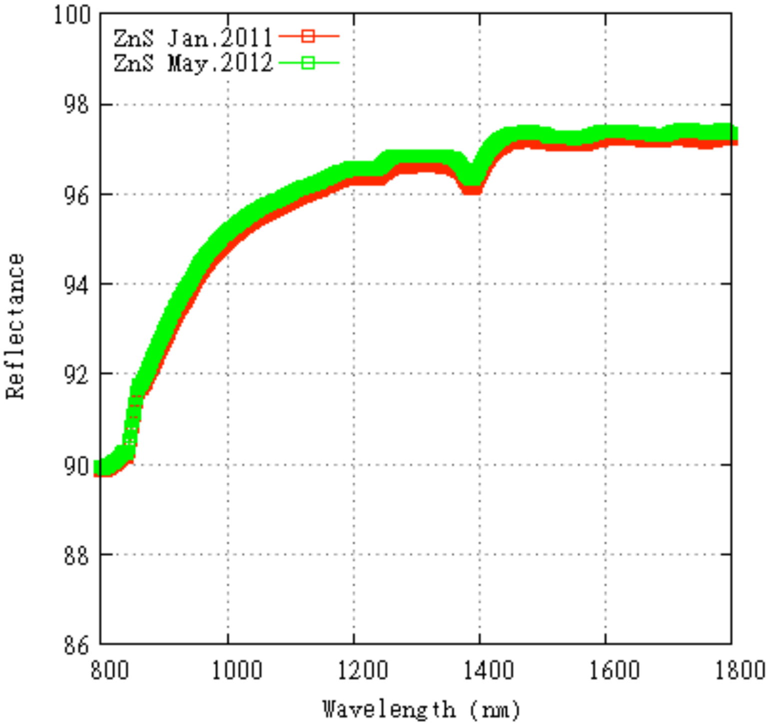

Figure 12. Comparison of immersed spectral reflectivity of SiO_2-Cu-SiC coating on a ZnS substrate before and after long term exposure to a humid environment. No significant change is noted.