Cryolite – a new look at an old standby

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Cryolite and zinc sulfide are a classic thin film pair for fabricating optical interference filters[1]. When this film system is laminated to a glass cover slip with index matching epoxy, the filters exhibit excellent environmental stability. These materials can be evaporated using resistive sources and as a result are a cost effective and rapid turnaround option for producing custom filters for prototyping and small lot size jobs. The high index contrast of cryolite (n= 1.3) and zinc sulfide (n= 2.3) provides a flexible design space and are typically used for bandpass filter or high/low pass filter designs with strong out of band blocking. The wide spectral range of the two materials allows for film designs from the near UV to beyond 10 microns. The materials are easily mixed to produce a range of intermediate index values. This provides a convenient way of tuning the width of the bandpass filter without complicating the design. We compare the properties of this film system with high performance oxide thin film materials.

1.0 Material Properties

Figure 1 presents a scanning electron microscope (SEM) image of a cryolite and zinc sulfide bandpass filter. The measured spectral scan for this film stack is presented in figure 2. The materials were thermally evaporated and the SEM image shows that the materials form smooth, dense layers. Each layer in the film was optically monitored and is an integral number of quarter waves at the design thickness of 682 nm.

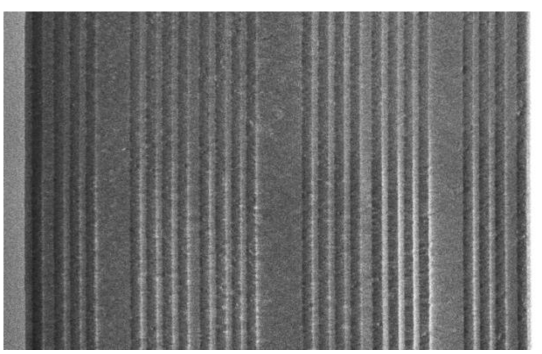

Figure 1: SEM micrograph of a cryolite/ZnS bandpass filter (Vanderbilt)

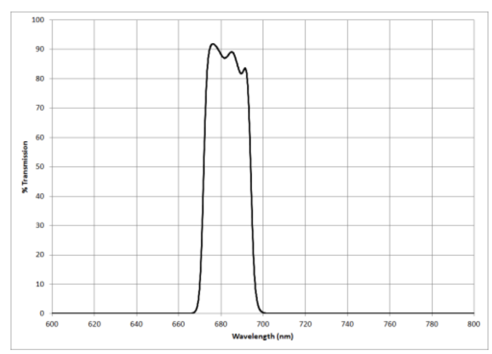

Figure 2: Measured transmission for the filter presented in figure 1.

1.2 Environmental Stability

Cryolite is sensitive to humidity if left unprotected. Lamination is an effective means of sealing the filter and making the cryolite/ZnS filter robust. Figures 3 and 4 present spectral scans of a filter made 33 years ago in 1983. The first measurement was made at the time the filter was fabricated. The second measurement was made recently in 2016. The filter shows no sign of degradation in either performance or cosmetics. Since the filters are laminated between glass, they are easy to clean and can tolerate rough handling.

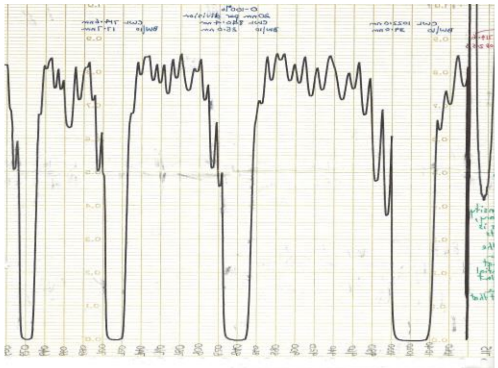

Figure 3 Transmission scan of a laminated rejection notch filter made 11/4/1983.

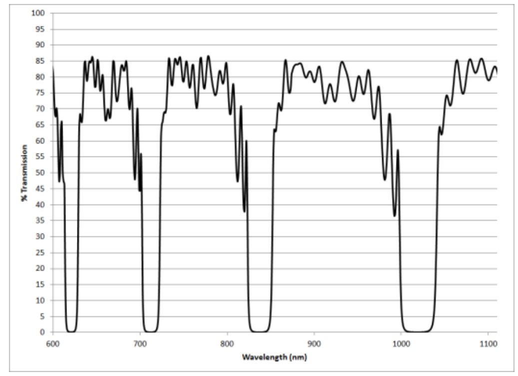

Figure 4: A recent Transmission scan the same filter made over 33 years ago demonstrates the filter's environmental stability.

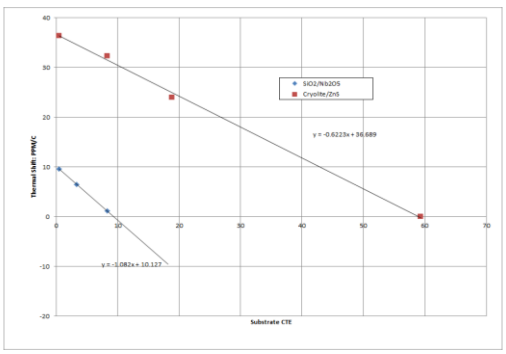

Figure 5: Measured spectral shift with temperature is presented for SiO_2/Nb_2O_5 (lower curve) and Cryolite/ZnS. The oxide film is thermally stabilized on a substrate with a CTE of 9.3. The Cryolite/ZnS filter is stabilized on a substrate with a CTE of 59.4.

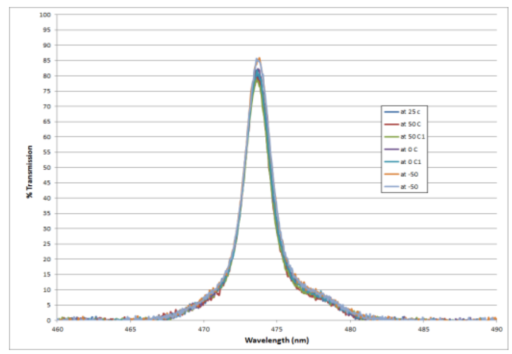

Figure 6: Measured transmission (normalized) of a Cryolite/ZnS bandpass filter on a high CTE substrate (polycarbonate) stabilizes the spectral shift with temperature.

1.3 Thermal Shift

Thermal shift is an important consideration for narrow (<5nm FWHM) and ultra-narrow (<1nm FWHM) bandpass filters. The degree of thermal shift has been shown to vary with the coefficient of thermal expansion (CTE) of the filter substrate[2, 3]. Thermal shift is measured for filters deposited on three different substrates glass types in the same deposition. The lower line in Figure 5 plots the measured shift in central peak wavelength versus the CTE of each glass for a SiO_2/Nb_2O_5. The zero intercept for this oxide filter is a substrate with a CTE of 9.3 ppm. The thermal shift of the oxide film on B270 is 0.22 nm over a temperature range of 100C. Figure 5 also plots the measured shift in central peak wavelength versus substrate CTE for a cryolite/ZnS filter deposited on three substrates. The zero intercept for this material system is a substrate CTE of 59.4 ppm. Materials in this CTE range include plastics. Figure 6 presents measured transmission for a laminated cryolite/ZnS bandpass filter deposited on polycarbonate. The thermal shift for this filter is 0.2nm over the 100 degree temperature range. This filter demonstrates that cryolite/ZnS filters can be thermally stabilized as well oxides, but the substrate needs to have a much higher CTE.

3.0 Application Example – All optical temperature sensor

A temperature sensor can be created by combining the thermal properties of both coating sets. Figure 7 presents a schematic of a laminated cryolite/ZnS short pass coating with a hard oxide, thermally stabilized long pass filter on the outside. The glass substrate is selected to thermally stabilize the oxide coating while the spectral performance of the cryolite/ZnS edge filter shifts with temperature. The result is an optical transmission which varies directly with temperature. The slope of the edge filter determines the sensor range and sensitivity. Figure 8 presents modeled transmission of the two edge filters. The solid lines present the transmission of each filter at 25 C. The dotted lines present performance at 75 C and -25 C.

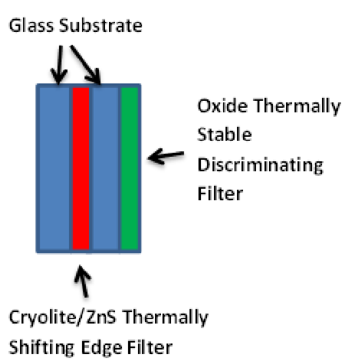

Figure 7: An all optical temperature sensor can be created by combining a laminated Cryolite/ZnS coating and a thermally stabilized oxide coating.

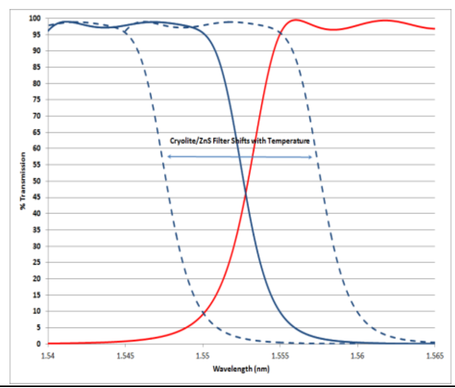

Figure 8: The laminated filter shifts with wavelength while the oxide filter is static

4.0 Conclusions

Cryolite/ZnS is a classical film system which is typically laminated. Once laminated, its performance is stable over decades. The high index contrast and wide spectral transmission range provide a design space from the UV through 10 microns. This film system remains a good choice for rapid prototypes and low cost, small lot production. Like oxide films, this film system can be thermally stabilized over a wide operating range of temperature and is a good candidate for coatings on plastics. Hybrid thin film devices using the properties of this film system with oxides provides the opportunity to create a variety of sensors. The example of an all optical temperature sensor is provided.

References

[1] Macleod, H. Angus; [Thin-Film Optical Filters (Optics and Optoelectronics Series) / Edition 4, 2010],

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[3] Sung-Hwa Kim and Chang Kwon Hwangbo, "Derivation of the center wavelength shift of narrow-bandpass filters under temperature change", Optics Express 5634, 15 Nov 2004.

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