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High performance AR coatings for germanium

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ABSTRACT

The theoretical design of a high efficiency antireflection coating on germanium for the 8 to 11.5 micrometer band is a relatively simple matter, but the reduction to practice of a high durability version of such a coating is not as easy. The first requirement is to reduce the reflection losses due to the very high index of refraction without adding significant absorptance or scattering. The second is to provide resistance to the environmental conditions which might be encountered by the product. The practical problems of stress and adhesion, hardness and abrasion resistance, and salt fog and humidity resistance pose some major challenges to the transformation from a design to a successful coating process. We describe some of our experiences with the evolution of the process from theory to practice, some of the problems encountered, and what we believe we have learned. Due to the extensive number of variables and the constraint on time and resources, the development could not be totally rigorous or exhaustive. The judgement and experience of the development staff was exercised to focus the resources on areas which were perceived to offer the best possibility of a solution to the requirements. The net result of the work described here was a process with considerably improved properties over the starting point of the development.

1. INTRODUCTION

Due to a limited number of coating chambers available to do a broad range of visible and infrared coatings on a daily basis, we have been confronted with the task of developing antireflection coatings for germanium which avoid the use of zinc sulfide and selenide. We believe these would lead to subsequent contamination problems if mixed with our normal visible coatings which are done at about 300 degrees centigrade using oxides, etc. We therefore have spent some time working with mostly thorium fluoride (ThF_4) and germanium (Ge) as coating materials. We have also been somewhat surprised to find that several established coating producers occasionally have problems meeting the more stringent requirements for AR's on germanium even with the use of the zinc materials. We have measured and environmentally tested examples from several well known vendors which do not truly meet all of the claims for durability and transmittance. We have, however, also tested one example from an unspecified supplier which does pass 24 hour salt fog, ten day plus humidity, and eraser rub testing. So we do know that it can be acheived. We here communicate some of our experience in this area (not all of which was positive).

2. DESIGN OF THE COATINGS

The designs of the coatings are relatively straightforward in terms of achieving the desired antireflection properties. Transmittance and durability is not as easy. Dobrowolski and Ho(1) studied a variety of designs in 1982. In previous papers(2)(3), we described the use of circle and/or admittance diagrams to easily visualize coating reflectance versus layer thickness. We showed how they can help the designer gain insight into monitoring sensitivity and other coating effects. These diagrams also lead to some very simple concepts for the design of broadband antireflection coatings on high index materials. Figure 1 shows the locus on an admittance diagram of a low index layer such as thorium flouride coated on a germanium substrate. This starts at the admittance of the germanium and proceeds to a minimum admittance which is not unity at the quarter wave optical thickness (QWOT) and then increases to the half wave point before repeating its path. Figure 1 also shows the admittance locus of a similar low index layer which passes through the admittance equal to 1.0 point or zero reflectance point in air or vacuum. These two locii are the key elements of this discussion. If only two materials are to be used in the AR coating of the substrate and this is the low material, there is a class of coatings where the first and last layers of the AR will lie on these two locii in a three layer coating. The only remaining task in the design of an AR will be to find the proper second layer to connect these two locii and optimize the broadband characteristics to suit the requirements.

Figure 2 shows the locii of a range of possible high index second layers which connect the two low index locii. It has been found that the proper choice of the connecting second layer gives a good achromatizing effect similar to that of the half wave second layer in the usual quarter-half-quarter wave (QHQ) designs for broadband AR's on glass. The use of the concept for coating germanium will be shown.

The circle/admittance diagrams like Figures 1 and 2 were used to select approximate layer thicknesses near the center of the desired AR band for an automatic optimization of layer thicknesses with respect to the coating requirements. Figure 3 shows the results of such an optimization of a ThF4-Ge-ThF4 coating on germanium. The solid line is the admittance locus for a wavelength near the center of the band, and the dotted lines are the circles for the two extreme wavelengths in the band. It will be seen that all of the circles terminate near the unity admittance or zero reflectance point. It can be seen that as the wavelength gets shorter or the layers appear to be longer, the end of the first layer moves the circle further toward the reflectance minimum point. The longer second layer moves its end point further from the real axis. Finally, the last layer must be longer (which it naturally is) to bring the final termination near the zero reflection point. The converse is true as the wavelength gets longer and the layers appear shorter. This compensation effect is what gives the achromatizing broadband performance desired. Figure 4 shows the reflection of the design over the required band.

3. APPLICATION OF THE DESIGNS

It seems to be possible but not easy to produce satisfactory antireflection coatings on germanium of the Th-Ge-Th type. It was found that careful attention had to be given to temperatures, rates, and pressures to keep stress, absorption, scattering, and durability under control.

Our experience indicates that adhesion is more an issue of stress control than any other factor. We had tried glow discharge before coating and found it somewhere between inconsequential and harmful to adhesion. We do not currently use glow discharge in these coatings. Temperature and rate seem most important. Van Uitert, et al.(4) of Bell Laboratories studied a single crystal of ThF4. They found that it has a negative coefficient of thermal expansion in the region of 25 to 300C. A brief matrix of tests which we did at an early stage recording absorption/scattering and the bending caused in thin substrates led us to the tenative conclusions that: 1) stress in ThF4 is least at higher temperatures when deposited in the 1 to 6xE-6 mbar range, 2) absorption and/or scattering are best at high rates and low pressures. We now start generally at 5xE-7 mbar. More current data also leads us to believe that stress is better in Ge-ThF4 stacks at higher deposition rates (15-60A/S), but definitely at higher temperatures. This seems to agree with the conclusions of Ennos(5). Getting low pressures at higher temperatures causes pumping time and cost challenges. However, we have been getting some indications that higher tempertures are associated with absorption or scattering in either the Ge or ThF4 or both. For some time we thought it was the ThF4 at temperatures over 250C, but we are now inclined to believe the germanium absorbs when deposited over 250C and ThF4 if over about 300C. We have had some success with changing temperature with layer number and even during a layer. Our favored process at the moment is three layer design where the last thick ThF4 layer is split into two nearly equal parts by a thin Ge layer making a five layer design. The design is seen in Figure 5. We described(6) the use of these very thin layers which have almost no effect on the design as ALMOST ACHROMATIC ABSENTEE (AAA) LAYERS. This seems to help both adhesion and transmittance. It may be that the thin layer is interupting stress build up and columnar structure growth. We have not had an opportunity to examine the micrographic structure. We find that we can increase the temperature after the thick Ge layer is deposited from about 245C to 300C without serious effect on the transmittance losses. Annealing at 300C or more for an hour seems to also help.

Because neither Ge nor ThF4 seemed to pass severe abrasion and salt fog tests in our early experience, small modifications of the basic design were tried. A thin overcoat of almost any index can be added as part of the last layer where its optical thickness is substituted for an equal optical thickness of the last layer. If the the layer is thin enough, its absorption in the pass band may be tolerable even if thick layers would absorb too much to be useful in the overcoating material. The compromise of "thick enough to protect" but "thin enough to transmit" is a key issue in an approach to producing high durability versions of the designed coating. Figure 6 shows the application of a thin isolating layer of Ge over the last ThF4 layer and then a thin layer for hardness on top of that. Note that the effects on the circle diagram are small and the spectral curve is not significantly different from that in Figure 4.

One of our first test runs to try to meet the severe abrasion requirements was a final layer of MgF2. This improved the resistance, but we have not yet been able to produce coatings with MgF2, CeF3, or NdF3 which meet the eraser rub and scotch tape test after 24 hour salt fog. We have also tried many of the common oxides as a hard outer layer. In thick enough layers, they meet the environmental resistance, but they then absorb too much to be useful. We have had some indication that the compliance or lack of hardness of the underlying layer may allow the top layer to crush and fail even though the top layer would be good on a firm substrate. SiO_2, Al_2O_3, and Ta_2O_5 show no sleeking when deposited on a germanium substrate, but on top of an AR coating, we have not been able to avoid fine sleeking. Any porosity also seems to allow attack by salt fog.

At the moment, we plan to continue refining the temperature and rate profiles of the processes for best transmittance and durability and the addition of thin protecting layers on top of the basic coating. We plan to publish some of these results and our analysis of other high durability AR coatings in early 1989.

4. CONCLUSIONS

The concept of the design of a three layer AR on high index substrates has been shown and is amenable to "back of the envelope" design, and it lends insight to what is happening in the design. The technique has proved useful to us in producing practical coatings on germanium for the 8 to 11.5 micron band. The reduction to practice of a high transmittance AR coating is well in hand, but a reliable high durability and high transmittance coating seems to be more uncommon than current commercial literature would lead one to believe.

5. REFERENCES

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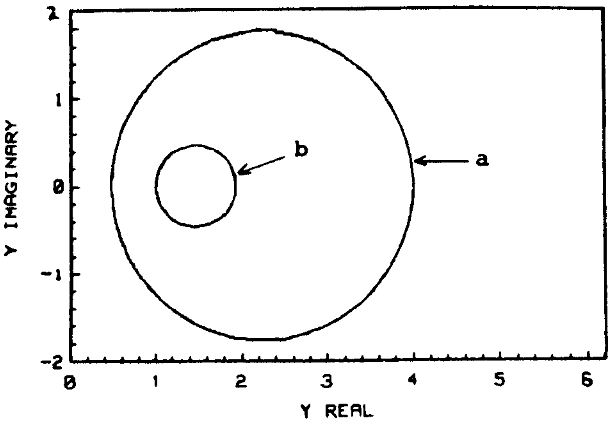

Fig. 1. Admittance diagram with: a) the locus of reflectance versus thickness of a ThF4 film on a germanium substrate. b) the locus for a ThF4 film ending in air or vacuum.

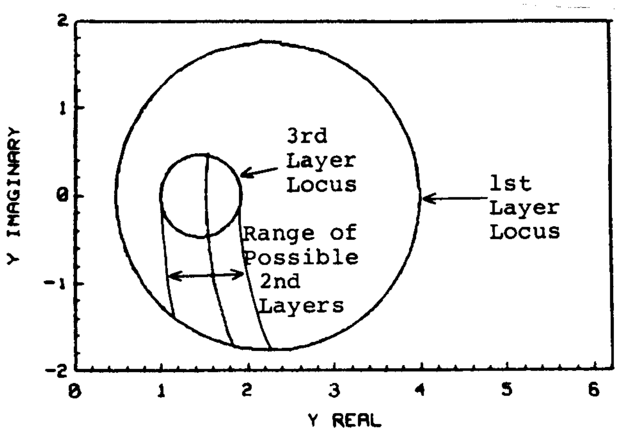

Fig. 2. Admittance diagram of possible high index (germanium) layers which could connect the two low index layers that start at the germanium substrate and end at the **admittance of a vacuum.**

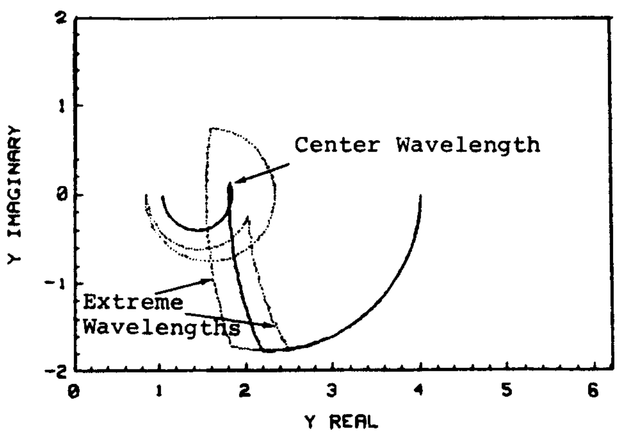

Fig. 3. Admittance of an optimized three layer AR of ThF4-Ge-ThF4 on germanium. Solid line is for a wavelength at the center of the band. Dotted lines are the long- and shortwave limits of the band.

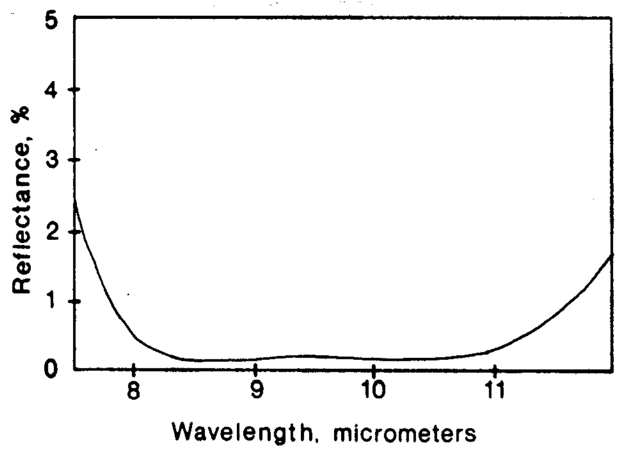

Fig. 4. Reflection versus wavelength of the optimized three layer design in Figure 3.

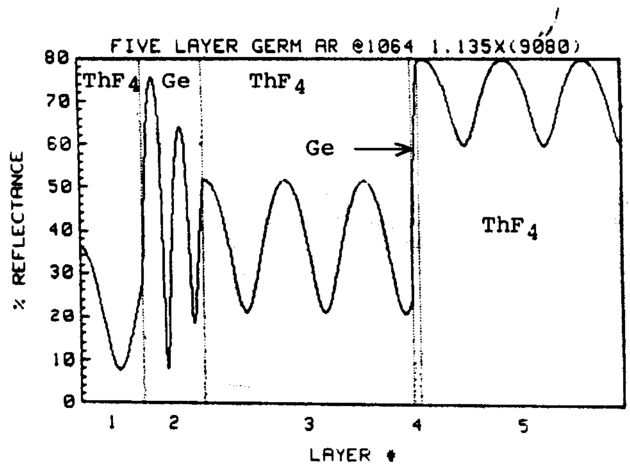

Fig. 5. Layer Thicknesses and optical monitoring curves at 1.064 micrometers of the currently preferred **AR** coating for germanium.

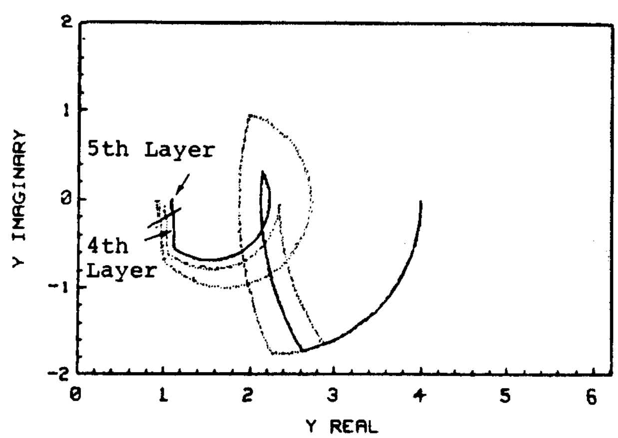

Fig. 6. Admittance diagram for a five layer AR with outer layers for hardening. Note the small extent of the 4th and 5th layers.