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Antireflection coatings for germanium without zinc

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ABSTRACT

We describe the concept, limitations, design, and application of a broadband antireflection coating for germanium which does not use zinc sulfide or zinc selenide. These materials have some undesirable working properties in production and it can be shown that their index of refraction limits the spectral performance which can be achieved. A design using only germanium and thorium fluoride can meet a broad range of requirements when stress and environmental durability are kept under control.

1. INTRODUCTION

The object of this work was to develop a broadband antireflection (AR) coating from 8 to 12 micrometers for Ge which could be produced in a chamber which is used for visible coatings on the same day. Zinc sulfide in particular is known to create "dirty" chambers which cannot readily be used for other higher temperature processes without extensive cleaning. We currently have a large number of visible processes which run in a relatively few chambers. This generates a desire to be able to mix visible and infrared coatings in the same chamber in rapid succession. Thorium fluoride and germanium were the principal coating materials chosen. These are known however to be difficult to control for stress and adhesion while simultaneously achieving good abrasion resistance and transmittance. Adequate temperature and rate control are critical to obtaining satisfactory films of the type which we require. ZnS and ZnSe are also undesirable as the low index component of a broad band antireflection coating. It will be shown from the literature and our own investigations that a lower index than ZnS is needed to meet the requirements for an AR on germanium that reflects an average less than 0.5% between 8 and 12 micrometers. Some of the experiences which we have gained in the development of this specific coating are described.

2. CONCEPT AND LIMITATIONS

The major concept used in the design of the coatings described here is that of the step-down layer system described by Jacobsson and Martensson(1,2) and by Dobrowolski and Ho(3). Figure 1 shows the index of refraction profile (curved line) of a single inhomogeneous layer which will act as a broadband antireflection coating between two media of low and high index at the two boundaries of the layer. Dobrowolski points out that the breadth of the AR band is proportional to the total physical thickness of the layer. Wavelengths shorter than that for which the layer is a half wave optical thickness will be antireflected. Jacobsson and Dobrowolski describe a variety of designs where the inhomogeneous layer is approximated by a stack of homogeneous layers of indices that "step-down" from the substrate to air or vacuum. We have taken a similar approach to gain some insight into the concept and limitations. Using automatic optimization to get as broad a low reflection region as practical, we varied only the indices of two, three, four, and seven layer stacks of quarter waves to find the ideal indices for that number of layers. Figure 1 has these steps of index shown for a step-down AR on germanium. The asymptotic approach of these index values to a curve is how we numerically derived the continuous curve of Figure 1. It is interesting to note that we get a rectilinear relationship between the index and the QWOT times the index of the QWOT through the layer stack. It is not yet clear to us what this might mean. Figure 2 shows the spectral performance achieved for each stack. Since the layers were all QWOTs at about 10 micrometers, it can be seen that the long wave limit moves out with total thickness (or number of layers). Figures 3, 4, 5, and 6 show the admittance diagrams of each of these designs. The admittance loci of the long and short wave ends of the bands are also shown.

The ability of a design to reach a low reflectance over a broad spectral region is inversely proportional to the lowest realizable index that can be used in the design. This was pointed out in reference 3 and by Aguilera, et al.(4) (which we will subsequently refer to as Baumeister because he and Dobrowolski actually wrote the paper including results from "et al"). This can be seen with the aid of Figures 5 and 6. The optimum broad design needs a final layer or layers which have an index less than those known or considered practical in conventional coating work. We would consider 1.35 a limit in our laboratory. These designs call for 1.157, 1.088, 1.263, etc. Although it is possible to simulate a lower index of refraction with a high index and an intermediate index layer for one wavelength, such a quasi-Herpin index solution will not work in the broad band required here. We inserted such a layer in the four layer design of Figure 5 as a substitute for the 1.157 layer and we let the program attempt to optimize it over the broad band. The result was that the design automatically converged to a last layer which was a QWOT of the lowest index real material used to make the Herpin index simulation. Although we have shown how any index can be simulated to any desired approximation by materials with indices that bound the desired index(5), we are not aware of any such solution outside the bounding indices. We then have to proceed with real designs whose last layer is of the lowest available index. The other indices can be replaced by Herpin equivalent index layers. We find that simple two layer pairs for each substitution are adequate in all of the designs considered here in accord with our earlier reported investigations(5). When the substitutions are made and the designs are reoptimized with only two materials (4.2 and 1.5 for Ge and ThF_4), the designs always converge to a last layer which is a QWOT of the low material at the design wavelength. The simplest case is the three layer coating originally designed from a different starting philosophy(6). Figure 7 shows this solution which is just a simulated index adaptation of the two layer system in Figure 3. Somewhat better spectral performance can be achieved by adapting the three layer design of Figure 4 with simulated layers (five) as seen in Figure 8. This gives only a modest reduction in performance from the ideal three layer toward the performance of the ideal two layer design. We found that dividing all but the last layer into two more layers for a total of seven and reoptimizing had little beneficial effect because of the constraint imposed by the index of the last layer not being as low as desired.

3. DESIGN

The comparison of numerical design methods by Baumeister, et al.(4) added to our insight with respect to the design problem at hand. They showed by example the limitation on the lowest reflectance by the lowest index and that the AR band gets wider as the total stack thickness increases. They found also that excess thickness beyond that required for the desired band serves to reduce ripple about the mean reflectance value. We followed this investigation by optimizing the five layer design of Figure 8 for various desired bandwidths. Figure 9 shows the results which are consistent with reference 4. The design chosen for the present application is the five layer of Figure 8 whose prescription and performance are shown in Figure 10. It was felt that the minor performance improvement offered by a seven layer design would be lost in manufacturing variances and would not be worth the extra production time and effort.

4. APPLICATION

Three examples of commercially available coatings were analyzed and found to be Zns/Ge/Zns/Fluoride. The last fluoride layer was ThF_4 in two cases and NdF_3 in the third case. Figure 11 shows the relative thicknesses of the layers in these designs and the one shown in Figure 10 which we have chosen. Figure 12 shows the admittance diagram of the NdF_3 version. Note that the second ZnS layer makes only a small adjustment in the admittance since its loci lie near the admittance of the ZnS itself. We believe that the ZnS was chosen because its stress tends to be the opposite(7) (compressive) of the fluorides and helps keep the average stack stress lower. As shown above, the low index fluoride is needed to get the average reflection below 0.5% in the 8 to 12 micrometer band. The thorium fluoride is also believed to offer more abrasion and other environmental resistance than the other materials. Our major challenge was to reduce the stress and increase the durability of the thorium fluoride layers. We performed a series of tests where the temperature and rates of deposition of ThF_4 were varied over a matrix of values from 150 to 325 degrees Celsius and 2-16nm/second. High rates and low temperatures resulted in high stress. We measured stress by the deformation caused in initially flat, thin germanium discs. Van Uitert(8) reported that ThF_4 has a negative thermal coefficient in the region of our measurements. This would imply that the differential expansion between Ge and ThF_4 deposited at elevated temperatures would tend to be compressive when cooled to ambient temperature. This would help to compensate an otherwise tensile condition. Low rates and high temperatures produced the best environmental durability. Mueller(9) reported modeling studies which indicate that slower deposition rates favor denser layer growth at lower temperatures than would be required at higher rates. This seems consistent with our observations of ThF_4. We had some absorption problems which turned out to be due to the Ge layers. Guenther(10) reported on the work of Evangelisti et al.(11) who found that germanium has a transition from amorphous to polycrystaline microstructure in a narrow range from about 240 to 280 degrees Celsius. This appears to have an attendant increase in absorption or scattering which shows dramatic losses in films deposited at too high a temperature. Our currently favored procedure is to apply the first four layers of the selected design at a substrate temperature of 200 degrees or less to avoid losses. We then raise the temperature to 325 degrees as the last layer is being deposited to increase the durability of the film. Preliminary tests with the inhomogeneous interface technique of Ledger(12) have been encouraging but not yet conclusive. We have not yet tried the "glue" layer approach of using HfO_2 as described by Oh(13) or Y_2O_3 as mentioned by Baumeister(4). We have also seen a commercial coating which has some (as yet unidentified) water repellent and hardening agent in the last layer which is very effective.

5. SUMMARY

The concepts and limitation demonstrations are key points of this paper. Design of the coatings follow in a straightforward way from the concepts. We have shared our experience to date with the application. The successful application mostly depends on the material properties that can be generated by the processes. We will therefore focus on the concepts and what insight might be gained. Several things can be seen from the ideal inhomogenious index profile of a single layer and the work of the referenced authors. The lowest index available, in the case of air or vacuum as a medium, limits the lowest reflectance that can be achieved over a broad band. The long wave limit of the band is proportional to the total thickness of the stack, and occurs where the wavelength is twice the thickness. Figure 6 is key to some of the insight which may be gained. The solid curve is the admittance at the longwave end of the AR band. It can be inferred that an infinite number of layers would lead to a continuous smooth curve near the path seen in Fig. 6. Beyond the longwave limit, the end of the locus moves away from the admittance point 1+i0 in the direction of lower values of the real and imaginary parts. It must ultimately return in an arc to the admittance of the substrate for wavelengths where the stack is a small part of a wavelength thick. The broken curve is the shortwave end of the band. The shortwave limit occurs as the descrete step-down layers approach one half wave optical thickness for that wavelength. At that wavelength, the admittance of each layer would return to its starting point at the admittance of the substrate and all layers would be "absentee layers". It appears that an infinitly divided stack would generate a smooth spiral pattern in the admittance diagram at all wavelengths in the AR band. We believe that this Figure 6 could be a minor sort of "Rosetta stone" to aid our understanding of ways to achieve broadband coatings that may lie obscured under layers of mathematical humus. We do not think we have yet deciphered all that may be gleaned from study of this type of curve and structure.

6. REFERENCES

1. R. Jacobsson and J. O. Martensson, "Evaporated inhomogeneous thin films," Appl. Opt. 5, 29 (1966).
2. R. Jacobsson, Progress in Optics, E. Wolf, ed. (North-Holland, Amsterdam, 1965), Vol. V.
3. J. A. Dobrowolski and F. Ho, "High performance step-down AR coatings for high refractive-index IR materials," Appl. Opt. 21, 288 (1982).
4. J. A. Aguilera, J. Aguilera, P. Baumeister, A. Bloom, D. Coursen, J. A. Dobrowolski, F. T. Goldstein, D. E. Gustafson, and R. A. Kemp, "Antireflection coatings for germanium IR optics: a comparison of numerical design methods," Appl. Opt. 27, 2832 (1988).
5. R. R. Willey, "Graphical description of equivalent index approximations and limitations," submitted to Appl. Opt. on 21 December 1988.
6. R. R. Willey, "High performance AR coatings for germanium," Thin Film Technologies III, K. H. Guenther and H. K. Pulker, SPIE Proc. 1019-25, Hamburg 1988
7. A. E. Ennos, "Stress developed in optical film coatings," Appl. Opt. 5, 54 (1966).
8. L. G. Van Uitert, et al., "Physical properties of thorium fluoride," Mat. Res. Bull. 11, 669 (1976), Pergamon Press.
9. K-H. Mueller, "Dependence of thin-film microstructure on deposition rate by means of a computer simulation," J. Appl. Phys. 58, 2573 (1985).
10. K. H. Guenther, "Physical and chemical aspects in the application of thin films on optical elements," Appl. Opt. 23, 3612 (1984).
11. F. Evangelisti, M. Garozzo, and G. Conte, "Structure of vapor deposited Ge films as a function of substrate temperature," J. Appl. Phys. 53, 7390 (1982).
12. A. M. Ledger, "Inhomogeneous interface laser mirror coatings," Appl. Opt. 18, 2979 (1979).
13. T. I. Oh, "Broadband AR coatings on germanium substrates using ion-assisted deposition," Appl. Opt. 27, 4255 (1988).

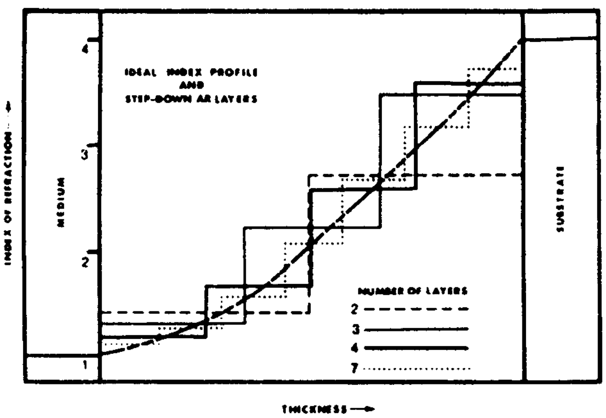

Fig. 1. Refractive index profile (curved line) of a single inhomogeneous layer for broadband AR on Ge. Discrete step-down layers of two, three, four, and seven layer designs.

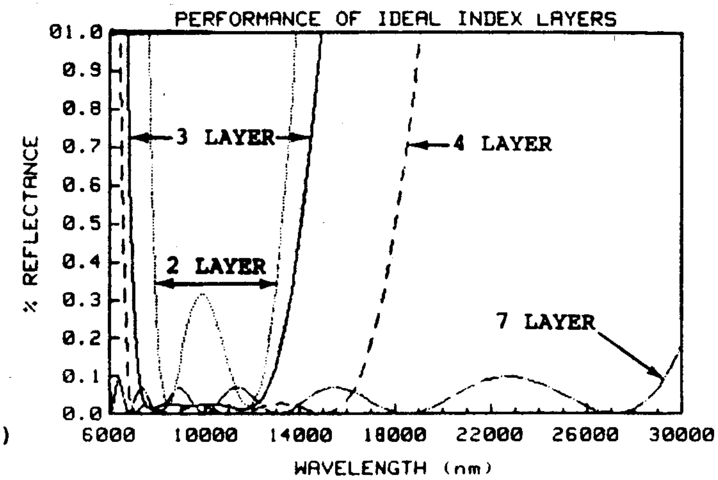

Fig. 2. Spectral performance of each of the ideal homogeneous step-down layer designs: 2, 3, 4, and 7 layers.

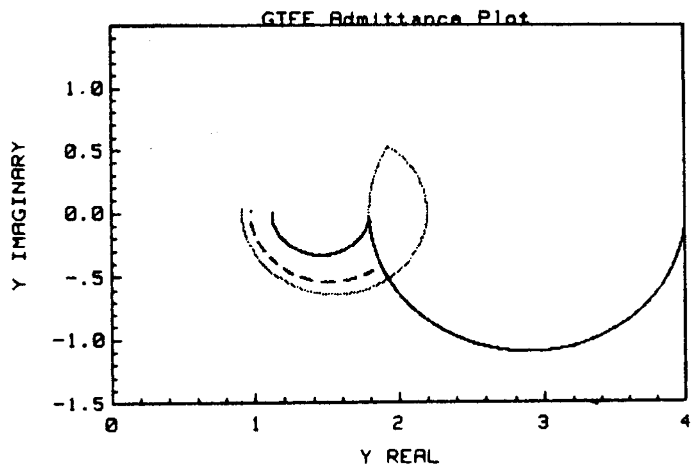

Fig. 3. Admittance loci for two layer step-down AR design at the central and two extreme wavelengths in the AR band.

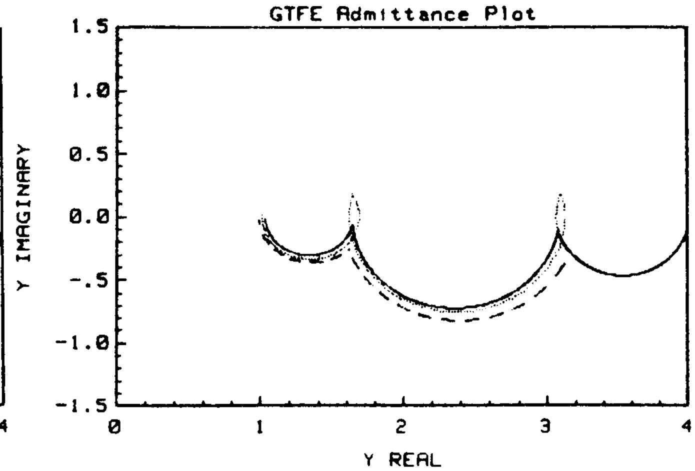

Fig. 4. Admittance loci for three layer step-down AR design at the central and the two extreme wavelengths in the AR band.

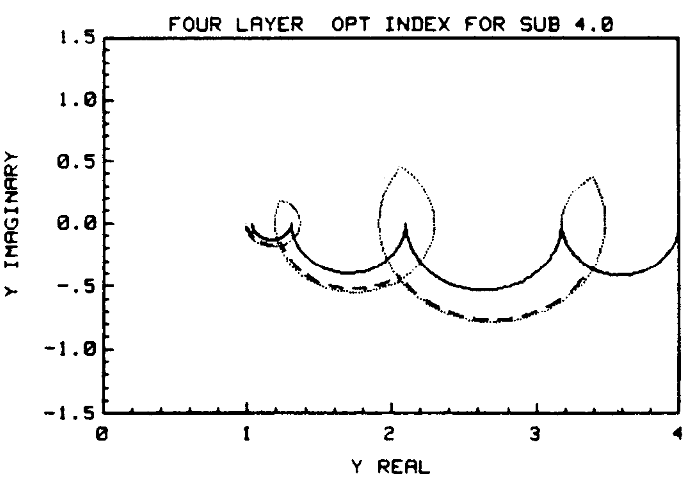

Fig. 5. Admittance loci for the four layer step-down AR design at the central and two extreme wavelengths in the AR band.

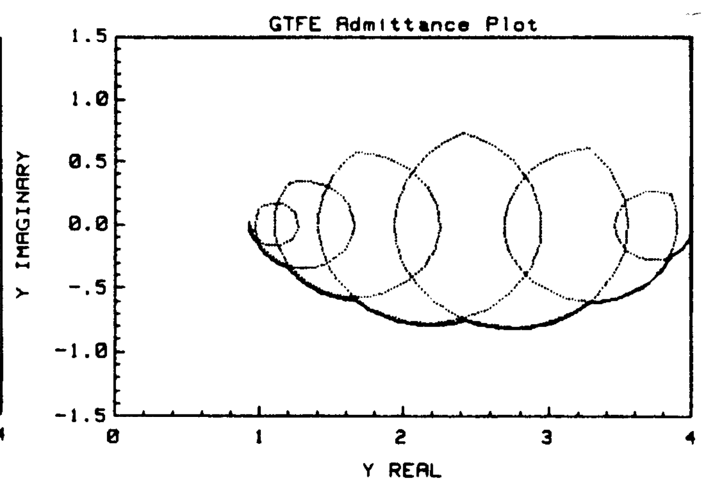

Fig. 6. Admittance loci for the seven layer step-down design at the two extreme wavelengths in the AR band.

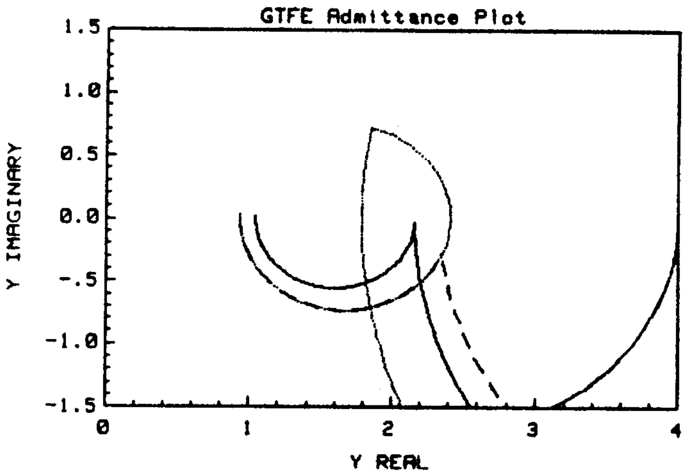

Fig. 7. Three layer AR which is an optimized equivalent index approximation of the two layer step-down design of Fig. 3.

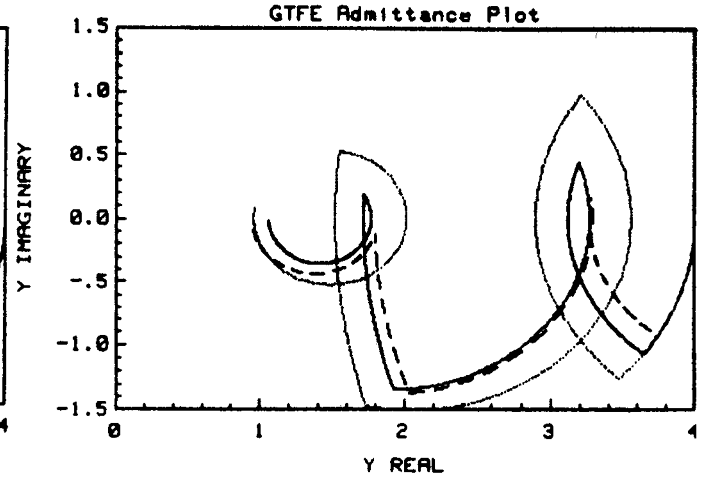

Fig. 8. Five layer AR adapted with equivalent index approximation from the three layer step-down design of Fig. 4 using optimization.

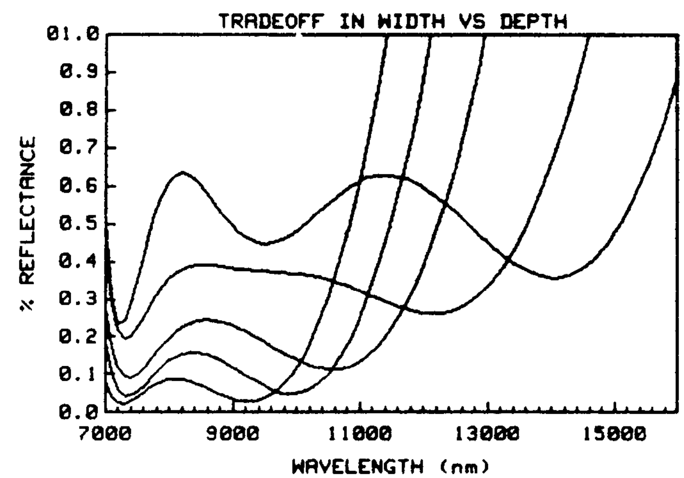

Fig. 9. Comparison of the results of optimizing the five layer design for progressively wider bandwidths. The degree of antireflection becomes compromised as the band widens.

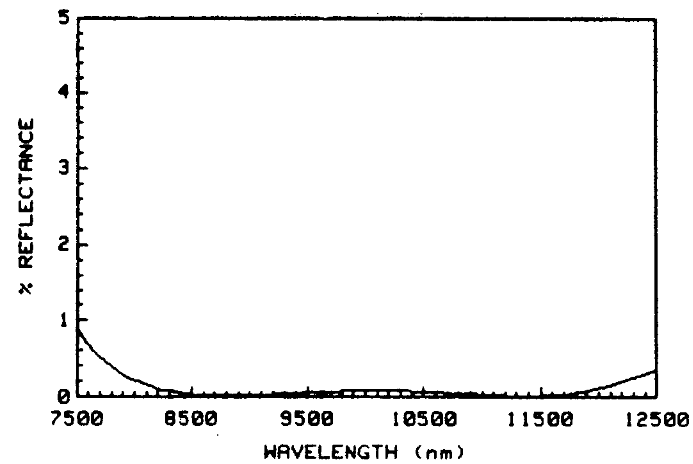

Fig. 10. Spectral performance of the five layer design of Figure 8. Design: H = Ge, L = ThF4, .065L/.473H/.264L/.243H/L .

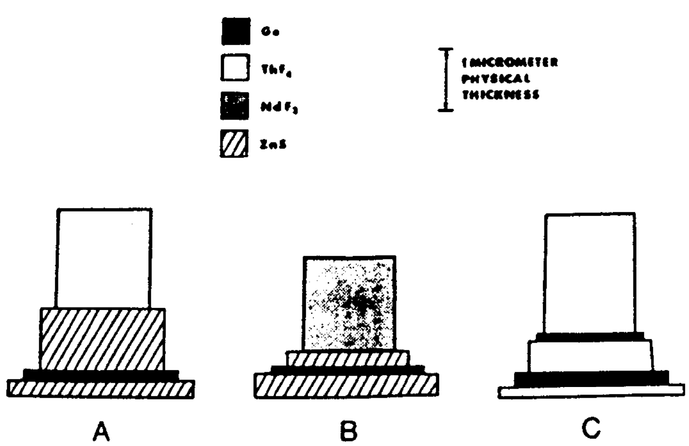

Fig. 11. Comparison of layer stacks for three different ARs whose goals are the same: A and B are commercial coatings, C is the zinc-free design of Figures 8 and 10

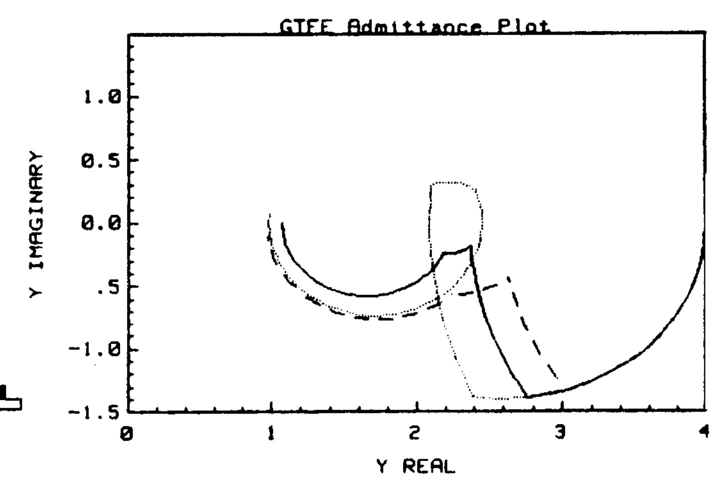

Fig. 12. Admittance loci of the ZnS/Ge/ZnS/NdF3 design in Figure 11.