Black layer coatings for the photolithographic manufacture of diffraction gratings

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A black layer coating for an aluminum–photoresist interface with a reflectance less than 0.1% for 413-nm, *s*-polarized light incident at 25° is described. It is made of space-compatible materials, and its rms roughness is less than 15 Å. © 2002 Optical Society of America

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1. Introduction

An efficient black layer coating is required for the manufacture of diffraction gratings with a holographic technique. In this process two *s*-polarized, 413-nm-wavelength laser beams impinge onto an aluminum substrate coated with a photoresist layer at an angle of 25° (Fig. 1). There they interfere to form a grating pattern in the photoresist. After exposure and etching, the photoresist is removed, prior to illumination, leaving a grating at the surface of the aluminum substrate. For a good process and to avoid problems resulting from thin-film interference, the reflectance at the substrate–photoresist interface must be reduced to as low a value as possible.[1] The resulting coating should withstand washing with acetone and caustic soda, solvents that are used in the manufacturing process. Because of the fine structure of the gratings to be fabricated, it is of further importance that the rms roughness of the surface of the black layer coating be less than 15 Å. It would be an advantage if the coating could be applied not only to aluminum but also to other substrate materials, such as Pyrex.

It is desirable that the reflectance of the treated interface be of the order of 0.1% and certainly less than 1%. In an alternative process a substrate made of black glass is used. There the reflectance of the glass–photoresist interface is of the order of 0.4% without any special treatment. However, there are mechanical and thermal reasons an aluminum substrate is preferable to black glass. Because the grating is part of an instrument that will be sent into space, the coating must be made of space-compatible materials and therefore must be stable for at least 2 years in that medium. Table 1 summarizes the specifications for the black layer coating.

2. Design

Solutions were sought that are based on the use of SiO_2 and Inconel (a Ni–Cr–Fe alloy), materials that the National Research Council of Canada has been using for many years for the manufacture of black surfaces used on space shuttle missions for the Canadian Space Agency. Coatings made of these materials are space qualified. They do not age significantly, and they withstand cleaning with acetone and caustic soda. In addition, they can be etched without problems. A thin, adhesive layer might have to be included to enhance the adhesion of the resist to the top SiO_2 layer.

It is well known (see, for example, Refs. 2–5) that black layer coatings based on thin-film interference consist of transparent, nonabsorbing materials and of thin, semitransparent metallic layers. The nonabsorbing layers are relatively thick, and errors in their thicknesses primarily result in wavelength shifts of the resulting coatings. To find a solution that is less sensitive to such thickness errors calls for design specifications with a low reflectance in the 390–450-nm spectral region, even though the reflectance needs to be low at only at 413 nm. These low-

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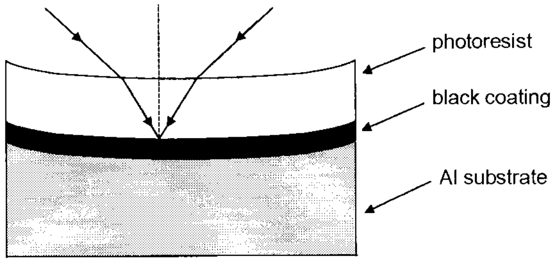

Fig. 1. Cross section of the required optical component.

reflectance values were specified for an angle of incidence of 25°, as measured within the photoresist.

Metallic layers, with the exception of the one deposited directly onto the substrate, are a few nanometers thick. Errors in their thicknesses cause a lack of the required balance between the amplitudes of the beams of light reflected at the various interfaces. This results in a reflectance higher than the nominal reflectance. The thicknesses of the thin metallic films critically depend on the optical constants of the experimentally produced layers.

Because of the difficulty of measuring the performance of the coatings and the lack of detailed information of the dispersion of the optical constants of the photoresist material, we decided to manufacture and measure two types of black layers: one for use with photoresist and the other for use in air.

Many different solutions with excellent properties can be found. Table 2 and Fig. 2 present three-layer (row a) and five-layer (row b) black layer solutions for a substrate–photoresist interface. The calculated reflectances (Fig. 2, first column) for *s*-polarized light incident onto the substrate at 25° (corresponding to approximately 48° in air) are well within the desired 0.1% throughout the specified spectral region. Also shown, in the second column of Fig. 2, are the refractive-index profiles of the three- and five-layer coatings. Very thin interface layers are at the metal–dielectric interfaces; these layers are discussed later. Similar systems with similar performances were designed for a substrate–air interface. The calculated reflectances, refractive-index profiles, and construction parameters of these systems are given in Fig. 3 and Table 2.

Table 1. Performance Specifications for the Black Layer Coatings

Specifications	Value
$R(\lambda = 413$ nm)	<1% (preferably ≤0.1%)
Angle of incidence	25° (at the photoresist–substrate interface)
Substrate	Inconel-coated aluminium
Ambient medium	Photoresist ($n \cong 1.7042$)
Rms roughness	<15 Å
Surface curvature	±5° on incidence angle
Other specifications	Space-compatible materials
	Should withstand acetone and caustic soda

Table 2. Designs for Black Layer Coatings for Use in Photoresist and in Air

	PHOTORESIST			AIR		
Layer	Material	Thickness (nm)		Material	Thickness (nm)	
Substrate	Inconel			Inconel		
1	SiO_2	124.6	129.0	SiO_2	328.4	790.7
2	Inconel	14.7	17.8	Inconel	20.6	45.2
3	SiO_2	467.9	360.4	SiO_2	312.4	347.6
4	Inconel		6.5	Inconel		19.9
5	SiO_2		227.4	SiO_2		323.0

3. Experimental Methodology

The multilayers presented in the previous section were produced on a dual-ion-beam sputtering (DIBS) system (Spector, Veeco-IonTech, Fort Collins, Colorado) with SiO_2 and Inconel 600 targets (PureTech Inc., Brewster, New York). It is well known that this process produces the dense and smooth coatings required for this application.

Several difficulties had to be overcome during the manufacture of black layer coatings of the type described in Table 2. These were related to the[6]

- Need for a very precise deposition of the thin metal layers;
- Thickness dependence of the optical constants of thin metal layers;
- Formation of an interfacial layer when a dielectric layer is deposited on top of a metal layer;
- Transmittance monitoring when the total metal thickness becomes significant; and
- Need for the precise characterization of the dispersion of the optical constants $n(\lambda)$ and $k(\lambda)$.

In addition, when the low-reflectance zone is located at short wavelengths, another difficulty is the precise characterization of $n(\lambda)$ and $k(\lambda)$ dispersions for all the coating materials used at the short wavelengths for which the black layer systems were defined.

A. Characterization of the Optical Constants

For light beams incident from the front and back sides, we determined n and k from *in situ* transmission data and from *ex situ* R and T spectrophotometric (Lambda 19, PerkinElmer, Shelton, Connecticut) and variable-angle spectroellipsometric (VASE; J. A. Woollam, Lincoln, Nebraska) data. Measurements were performed on single films and multilayers. The results are shown in Fig. 4. The error in the estimation of the index is believed to be less than 0.05, although it could be higher in the case of very thin layers.

The optical constants of Inconel [Figs. 4(a)–4(c)] depend on the thickness of the layer. These values were used during the design of the system. Also shown are the optical constants of SiO_2 [Fig. 4(d)] and amorphous silicon (a-Si) [Fig. 4(f)] deposited in our DIBS system.

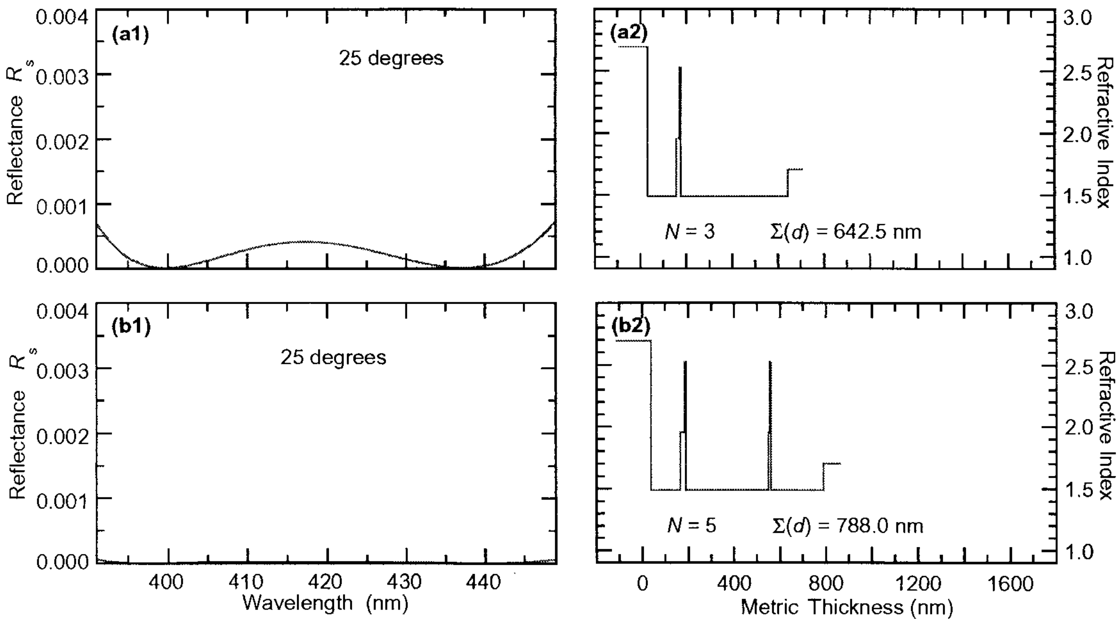

Fig. 2. Calculated reflectance and refractive-index profiles of three- and five-layer black coatings for a substrate–photoresist interface.

B. Oxidation of Inconel

On the basis of *in situ* transmittance measurements, we noticed that Inconel oxide layers (approximately 4.5 nm thick) were formed on top of the Inconel layers during the subsequent reactive deposition of SiO_2 [Fig. 5(a)]. The amount of Inconel removed owing to the oxidation ranged from 2.0 to 2.8 nm, depending on the layer. The optical constants found for the very thin layer of Inconel oxide are shown in Fig. 4(e).

There are two different ways of dealing with this problem. One way is to deposit Inconel layers of thicknesses that have been adjusted for the expected loss of metal owing to the oxidation. It is also necessary to adjust the thicknesses of all the layers of the system to optimize the performance of the system containing the very thin interfacial Inconel oxide layers. These are the thin Inconel interface layers that can be seen in the refractive-index profiles of Fig. 2. Another way of obtaining the correct Inconel layer thicknesses is to protect them with very thin a-Si layers deposited in an Ar residual atmosphere. The measured optical constants of this material are shown in Fig. 4(f). If the thickness of the layer is correctly chosen, it will be completely oxidized during

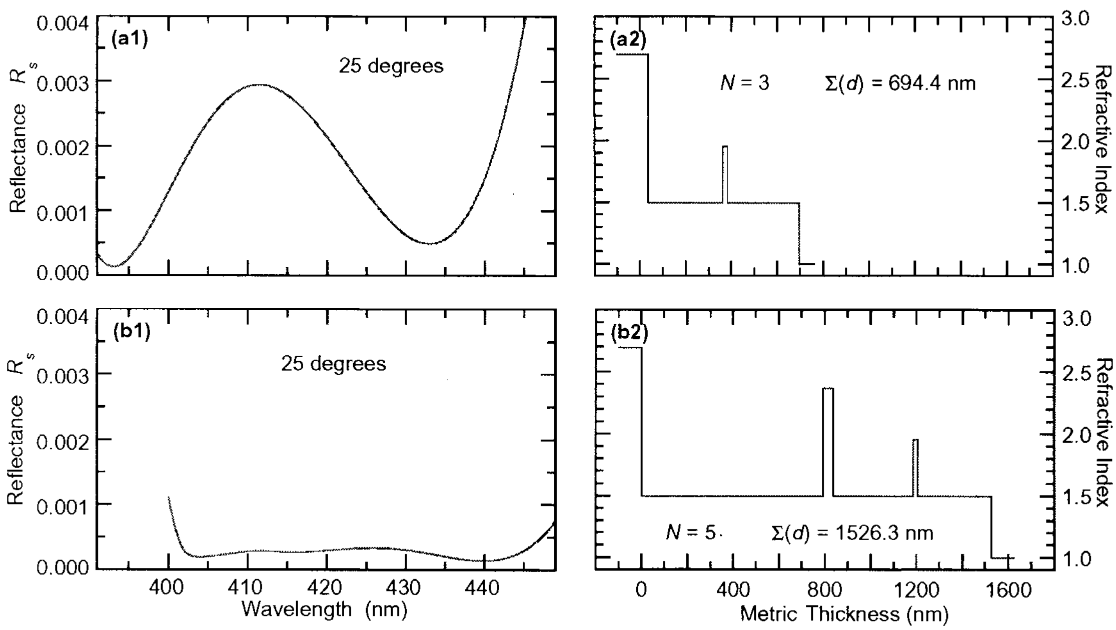

Fig. 3. Calculated reflectance and refractive-index profiles of three- and five-layer black coatings for a substrate–air interface.

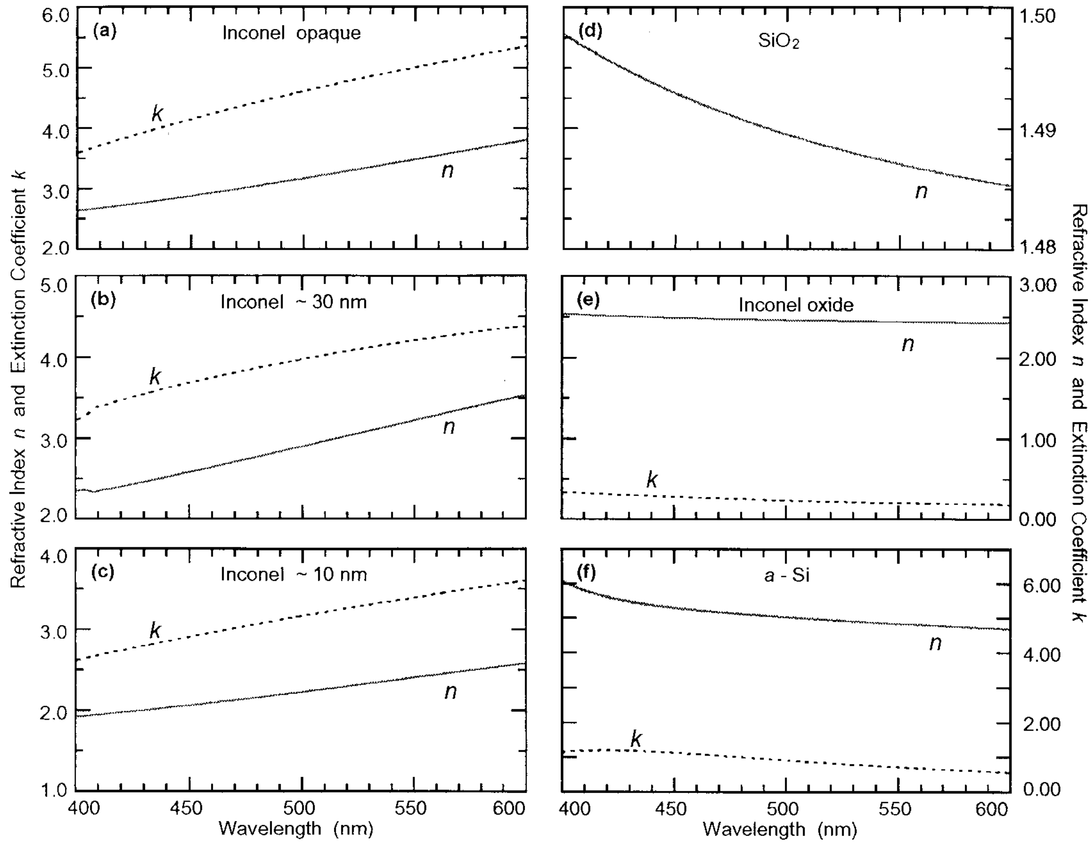

Fig. 4. Measured optical constants of all the materials used in the manufacture of the black layer coatings (a)–(c) Inconel layer with different thicknesses, (d) SiO_2, (e) thin Inconel oxide, (f) thin a-Si.

the subsequent SiO_2 deposition and will become an integral part of that layer. This approach, shown schematically in Fig. 5(b) was used in the designs of Fig. 3.

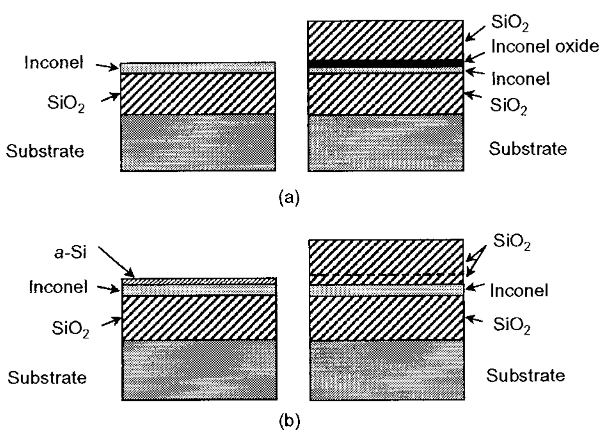

Fig. 5. Two different approaches to overcoming the effect of the oxidation of Inconel layers. (a) Compensation for the loss of Inconel thickness and adjustment of layer thicknesses to allow for the presence of Inconel oxide interfaces. (b) Prevention of the formation of the Inconel oxide layers by the deposition of a thin a-Si layer in an Ar residual atmosphere.

C. Sensitivity

We used *in situ* transmittance measurements to determine the thicknesses of all the layers deposited. Because the substrates were opaque, it was necessary to use glass witness slides for the monitoring. Further, because the transmitted signal was reduced, the layer thicknesses were determined with smaller precision as the total thickness of metal in the coating increased.

The performances of the designs were sensitive to the layers thicknesses. Figure 6 illustrates, for the five-layer black coating design for the substrate–air interface (Fig. 3 and Table 2, columns 5 and 7), the sensitivity of the system to small-thickness changes in the various layers. The first column of Fig. 6 shows the sensitivity to small-thickness changes in each layer of the calculated transmittance at the end of the monitoring process. The second column of Fig. 6 shows the calculated performance of the completed coating for the same thickness changes. In these calculations it was assumed that the thicknesses of all other layers except the one under consideration were correct. We will show that the sensitivity of the thickness determination during monitoring is low for the final three layers and especially for so the last one (first column). It is very difficult to deposit these layers precisely, and this has

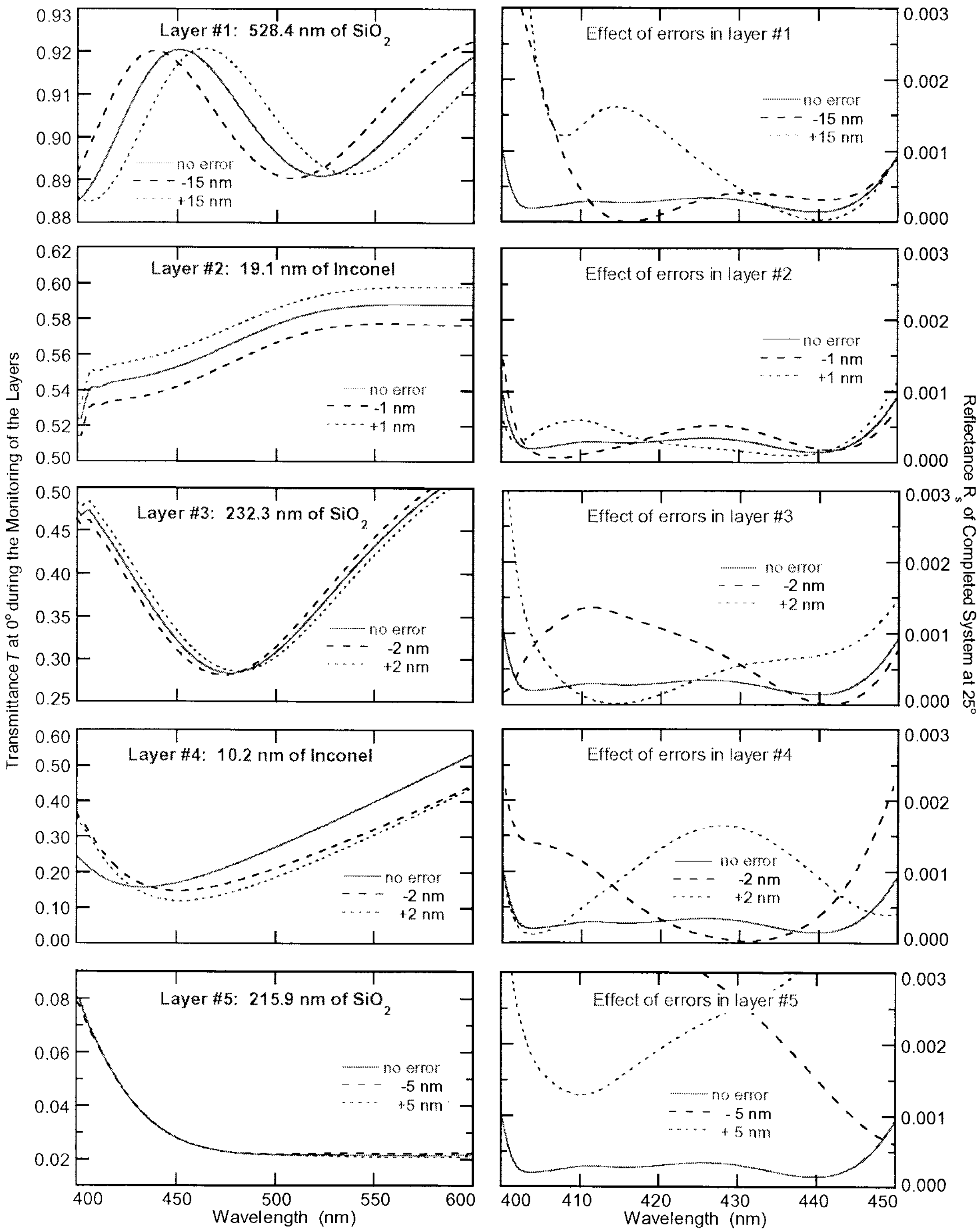

Fig. 6. Thickness-determination sensitivity and performance sensitivity for each layer of a five-layer black coating in air. The graphs in the left column show calculated transmittance spectra simulating optical monitor measurements for each layer and how they are affected by an error in the layer thickness. The graphs in the right column show the effect of these errors on the final coating performance.

a serious effect on the performance of the finished coating (second column).

To enhance the precision of the thickness determination, we subdivided the five-layer coating into two parts, and we used two different monitoring slides. The first three layers were monitored on the first slide, and the remaining 2 layers were monitored on the second slide. To increase the precision of the thickness determination of the first SiO_2 layer, the first monitoring slide was made of F7 glass or of a B270 glass that was precoated with Inconel.

4. Results

We used the two different strategies described above to fabricate black layer coatings for substrate–photoresist and substrate–air interfaces. In partic-

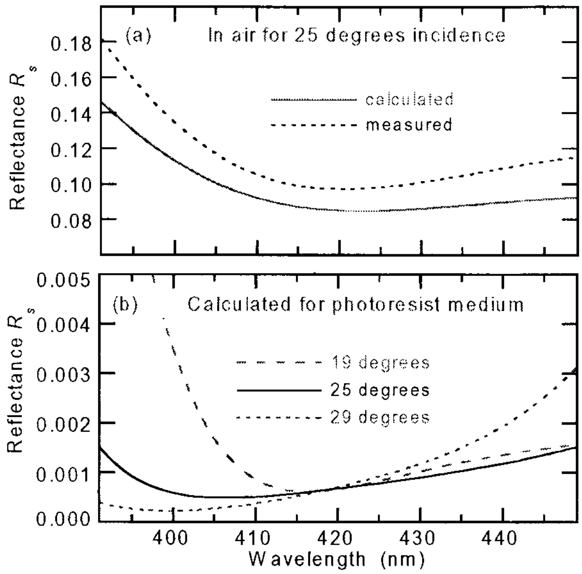

Fig. 7. Experimental measurements on the black coatings for use in photoresist. (a) Measurement in air. (b) Estimated performance.

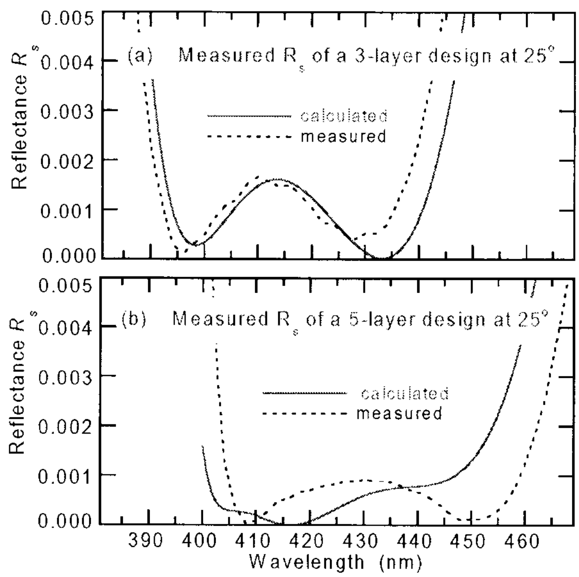

Fig. 8. Experimental measurements on the black coatings for use in air. (a) three-layer and (b) five-layer coatings.

ular, we designed the coatings for use with photoresist, assuming that thin Inconel oxide layers were present. Protective *a*-Si layers were used in the fabrication of the coatings designed for use in air. In addition, all the aluminum substrates were precoated with a thick Inconel layer, with known optical properties.

Precise measurement of the optical performance of the coatings was difficult. We used a spectroellipsometer to measure the *s*-polarized light reflection in air at 25°, R_s [Fig. 7(a)]. Figure 7(b) shows, on the basis of measurements made in air, the estimated performance of the five-layer black layer for use with photoresist. The performances of the three- and the five-layer black coatings for use in air were measured and are shown in Figs. 8(a) and 8(b), respectively. Although the performances of the coatings met the requirements, differences between expected and measured values of R_s exist. They were attributed to errors in the optical constants used in the designs.

5. Conclusion

We found that manufacturing a black layer coating with a reflectance of less than 1% was easy. However, achieving a reflectance of less than 0.1% in a wide wavelength range was difficult. The coating performance strongly depends on the optical constants of the coating materials, and these are difficult to measure at low wavelengths. Nevertheless, we succeeded in fabricating very efficient black layer coatings that met the requirements outlined in Table 1.

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