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Spectroscopic Ellipsometry as a Sensitive Monitor of Materials Contamination

Jeffrey S. Hale, James N. Hilfiker, Blaine Spady, Ron Synowicki, and John A. Woollam
Center for Microelectronic and Optical Materials Research, and Department of Electrical Engineering, Lincoln NE, 68588-0511

Abstract:

Spectroscopic ellipsometry is demonstrated to be extremely sensitive to contamination layers in the thickness range from 0.1 nm to 10 microns. In the present experiments we deposit either a thin lubricating oil (WD-40) or mineral oil continuously onto Ir, Cu, Al, Au, and V substrates from a bubbler, and monitor its thickness growth from sub-nanometer to tens of nanometers as a function of time. Re-evaporation of contaminant oils is also monitored in real-time by ellipsometry.

Introduction:

Ellipsometry at one wavelength has been used for many years to determine thickness of SiO_2 on Si for example. Recently spectroscopic ellipsometry has been developed in which a wide spectral range enhances the analytical power of the instrument enormously. Secondly, spectroscopic ellipsometers can now be built which acquire data extremely rapidly. For example, the JA Woollam Co. "M-44" ellipsometer acquires data at 44 simultaneous wavelengths in approximately 40 msec. Thus one can monitor processes in real-time.

NASA plans to launch an X-ray telescope using Iridium metal surfaces for mirrors. Extremely thin layers of contaminants will have an enormous effect on the performance of the telescope. This paper demonstrates the sensitivity of spectroscopic ellipsometry to contaminant layers as thin as 0.1 nm (and as thick as 10 microns).

Ellipsometry uses polarized light incident at an oblique angle (typically 70° to the normal) to the material under study. The reflected light polarization state is analyzed to determine the thickness, composition and properties of the film under study. Spectroscopic ellipsometry has been used on multilayer materials to determine thicknesses and compositions of ten and more layers. Thus it is an extremely powerful thin film diagnostics tool.

Experiment:

Substrates used in these experiments were prepared by magnetron sputter deposition from high purity targets of the elements Ir, Cu, Al, Au, and V. These films were approximately 100 nm thick, great enough that the films were considered to be "optically thick"; that is, light could not penetrate through to the silicon substrate.

The oils used in this experiment were WD-40 (a general purpose light lubricating oil) and mineral oil. These oils were deposited onto freshly prepared thin-film samples by bubbling air through a beaker containing the oil as shown in Figure 1. The bubbler worked by flowing clean air into a beaker of oil through a piece styrofoam with several pinholes in it to produce small bubbles. The air suspended oil

was then transported to a sample while an ellipsometer continuously acquired data. This provided real time data from which the optical properties and thickness of the deposited oil were determined. A variable angle spectroscopic ellipsometer (VASE) was used to monitor the growth of mineral oil on Ir, Cu, Au, and Al; and a 44 wavelength fixed angle ellipsometer was used to monitor deposition of WD-40 on V. A WYKO Rough Surface Tester was also used to try to see evidence of contamination of the samples before and after the WD-40 oil depositions.

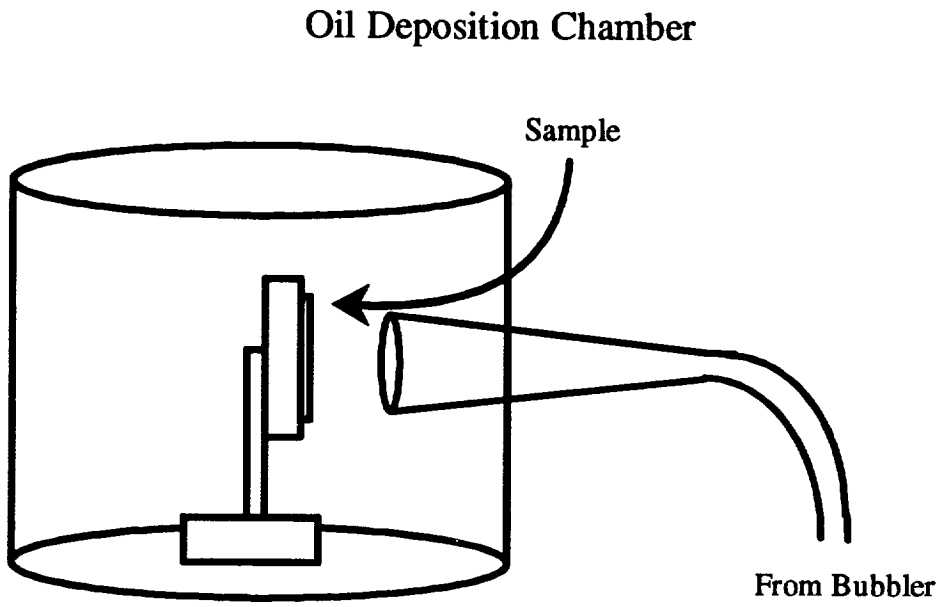

Figure 1. Oil deposition chamber that mounts on the ellipsometer.

Results and Discussion:

The optical constants for the mineral oil were found by depositing 50 nm of oil on Al and then taking VASE data at three angles of incidence. The data fits and optical constants are shown in Figures 2, 3, and 4. A Cauchy dispersion model was used to model the optical constants. These optical constants were then used while monitoring the growth of thin films of mineral oil on Ir, Au, and Cu. The film growth in some cases was not strictly linear in time due to insufficient control of the air flow rate. Spectroscopic ellipsometry data measured during growth showed the film thickness increasing slowly on a sub- monolayer scale. The depositions on Ir and Au were observed as the films grew from 0 nm to around 3 nm (Figure 5 and Figure 6), and the film on Cu was observed as it grew from 0 nm to 8.5 nm (Figure 7).

The bulk optical constants for WD-40 oil (Figure 8) were found by taking ellipsometry data on the oil in a beaker. When using these constants for the oil films, 13% void had to be added in an effective medium mixture model to get good fits to the data. This is likely due to some air being trapped in the film as a result of the bubbler acting as an aerosol. When the bubbler was turned on, a thin layer of oil was rapidly deposited on the Vanadium sample. After the initial layer was deposited the growth rate slowed to around 0.007 nm/sec. When the bubbler was turned off, most of what was deposited evaporated within about one minute leaving only a small additional layer of oil on the surface. Longer depositions resulted in a thicker film being left on the sample after the flow was stopped and re-evaporation took place. Several depositions were done on the same sample so this evaporation could be observed.

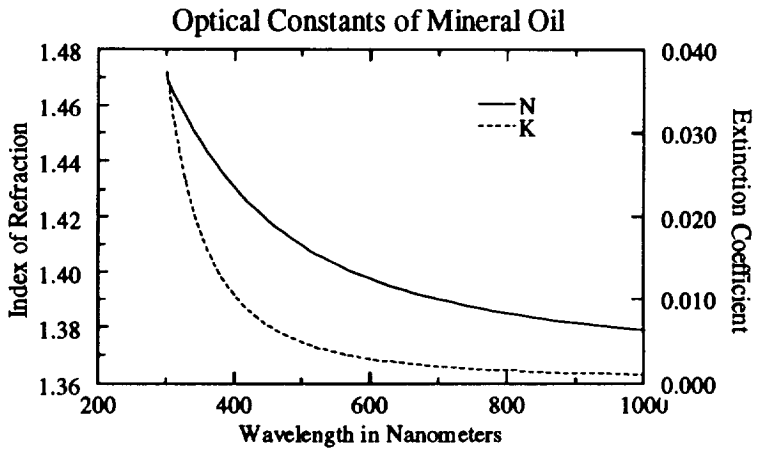

Figure 2. Optical constants of mineral oil modeled with Cauchy dispersion model.

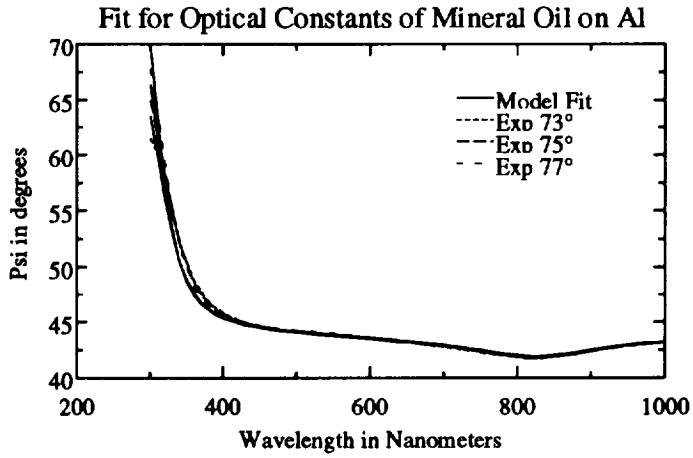

Figure 3. Ellipsometric psi data from fit for optical constants of mineral oil on Al.

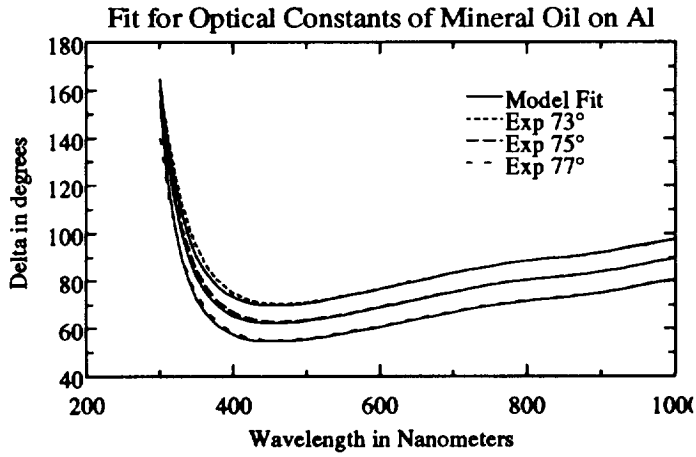

Figure 4. Ellipsometric delta data from fit for optical constants of mineral oil on Al.

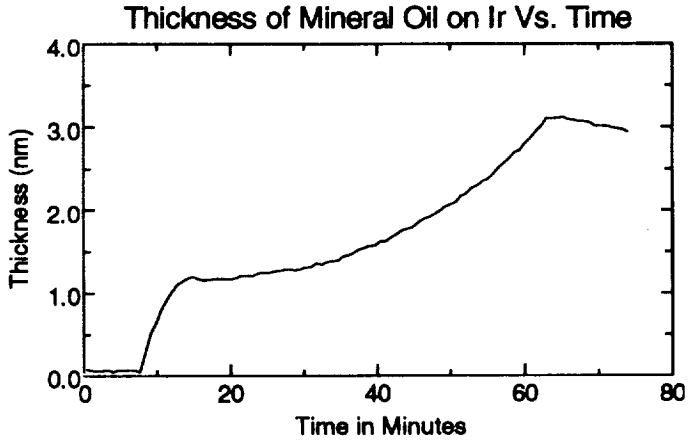

Figure 5. Thickness of mineral oil deposited on Ir thin film versus time.

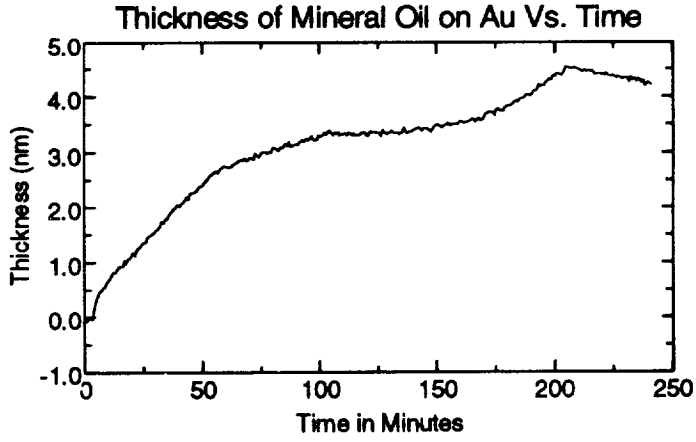

Figure 6. Thickness of mineral oil deposited on a Au thin film versus time.

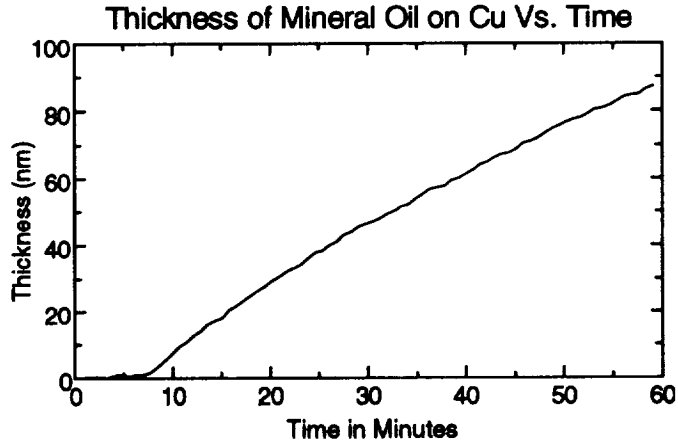

Figure 7. Thickness of mineral oil deposited on a Cu thin film versus time.

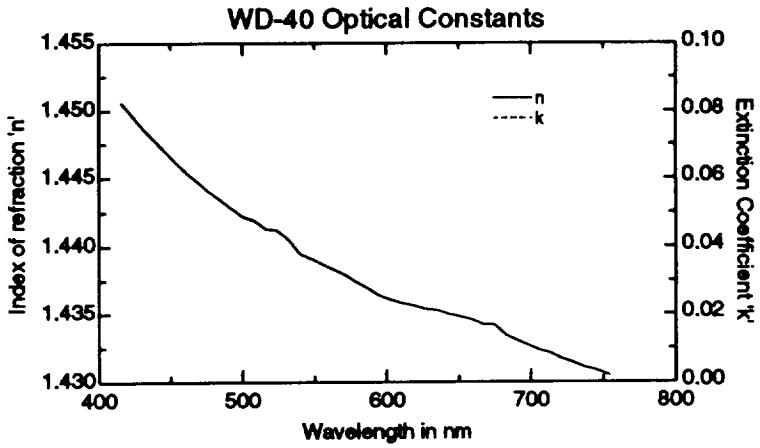

Figure 8. Bulk optical constants of WD-40 found by taking ellipsometry data on oil in a beaker.

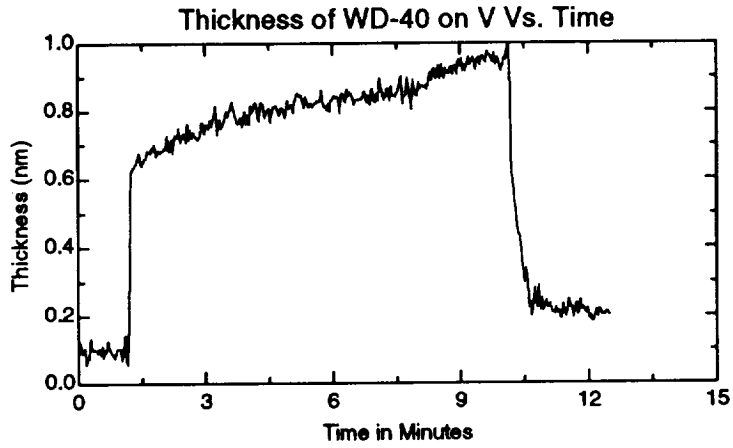

Figure 9. Thickness of WD-40 on V during second oil deposition

WYKO data were also taken before and after the depositions to observe the contamination, but no changes in surface morphology were observed. The first deposition was for 1 minute and the resulting film was only 0.1 nm thick. The second deposition was for 10 minutes, and the ellipsometric data for this deposition are shown in Figure 9. During the 10 minutes an initial film thickness of 0.45 nm was deposited before the growth rate slowed. Just before the bubbler was turned off the film thickness had reached 0.75 nm. After the bubbler was turned off, the film left on the surface was 0.2 nm thick. A third deposition was done for 20 minutes. The film thickness just before the bubbler was turned off was 1.8nm and after it was turned off the thickness was 0.6 nm. By the final deposition the thickness before the bubbler was turned off (after 4.5 hours) reached 11.5 nm and the thickness after the bubbler was turned off was 4.5 nm. Thus the oil film steady-state layer thickness grew as a function of deposition time. Likewise the post-bubbler (long-term) thickness was greater the longer the steady-state deposition was carried out.

Conclusions:

Several general conclusions can be made: these experiments demonstrate the enormous sensitivity of spectroscopic ellipsometry to levels of contamination representing less than 0.1 nm thick layers. Based on our measurements, these levels are apparently below the level detectable by the WYKO microscope. Our experiments were not carried out for long enough to determine when there was sufficient film thickness for the WYKO instrument to be useful, but based on our measurements this will be at least greater than 9 nm thickness. The ellipsometric measurement of sub-nanometer contamination involves only a beam of visible light so the surface is undisturbed. The only other technique with possibly sub-nanometer sensitivity is Auger spectroscopy, which involves use of ultra-high vacuum and small area surfaces. Auger determines the constituent contaminants but not their layer thicknesses. Ellipsometry can be set up to inspect large surface areas in any ambient environment and with sub-nanometer thickness sensitivity to contamination.

The present experiments were done using visible light. We have recently constructed a mid-infrared (2-14 micron) infrared ellipsometer which can be used to help identify contaminant species by identifying the frequency and strength of resonant-like vibrational spectra.

References:

1. J.A. Woollam and P.G. Snyder, "Variable Angle Spectroscopic Ellipsometry", book chapter in Encyclopedia of Materials Characterization, Butterworth-Heinmann Publishers, Boston, page 401 (1992).

2. J.A. Woollam, P.G. Snyder, H. Yao, and B. Johs, "In-situ and Ex-situ Ellipsometric Characterization for Semiconductor Technology", SPIE 1678, 246 (1992).