Japanese Journal of Applied Physics

Sensitivity Enhancement by Sample Surface Coatings on Photothermal Metal Thin-Film Thickness Measurements

To cite this article: Yoshitsugu Okamoto *et al* 2005 *Jpn. J. Appl. Phys.* **44** 4394

Japanese Journal of Applied Physics
Vol. 44, No. 6B, 2005, pp. 4394–4398

Sensitivity Enhancement by Sample Surface Coatings on Photothermal Metal Thin-Film Thickness Measurements

Yoshitsugu OKAMOTO*, Atsushi YARAI and Takuji NAKANISHI

Department of Electrical Engineering and Electronics, Faculty of Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito, Osaka 574-8530, Japan

(Received November 9, 2004; accepted March 5, 2005; published June 24, 2005)

An effective and stable method to enhance the sensitivity for photothermal measurements was proposed. The effectiveness of our method was proven by measuring the thickness of metal thin-film samples. It features sample surface coatings to improve the pumping beam's absorption of the sample as well as radiation efficiencies from the sample. Two solutions, graphite and dye, were used as coating materials. As metal thin-film samples, aluminum films formed by vacuum deposition on sapphire substrate were used. The inclination of the line showing the relationship between detection signals to the aluminum film thickness (i.e. measurement sensitivity) with coatings is more than three times larger than without coatings. Resolution on the order of a few nm film thickness measurement was achieved by using this coating method for metal films whose thickness ranged from 0 to several hundred nm. The effectiveness of our method functions for other photothermal measurements.
[DOI: 10.1143/JJAP.44.4394]

KEYWORDS: photothermal technique, infrared radiometry, sample surface coating, metal thin-film thickness measurements

1. Introduction

As sensitivities for photothermal measurements are generally quite low, methods for enhancing sensitivity are usually very important. From this standpoint of view, an effective and stable method to enhance sensitivity for photothermal measurements was proposed. The effectiveness of our method was proven through metal thin-film thickness measurement examples. The thickness of conductive metal thin films used in such devices as LSI chips has recently reached the order of about several ten to a few hundred nm. Accordingly, demand is strong for a simple method to measure thickness with high resolution. Although various photothermal detection methods satisfy such objectives, the reflection of the pumping light beam on the sample surface decreases the photothermal conversion efficiency, which causes low measurement sensitivity.

There are commercial instruments to measure thin film thickness such as 1) surface profiler, 2) interferometer, 3) ellipsometer, and so on. But all are quite expensive and complicated to use; moreover, these instruments have their own demerits for measuring thin metal films: 1) is not a nondestructive measurement instrument; 2) cannot measure opaque films; and 3) needs photonic parameters of film and substrate like refractive indices.

On the other hand, high measurement resolution was obtained for thin-film thickness measurements by a photothermal method.[1] But the method's instrument has disadvantages similar to other photothermal methods; it is very complicated and expensive; thickness is unobtainable if the quality of the film is uneven for various thickness samples, as well as unobtainable without material constants of the films; and obtaining wide aerial average film thickness is difficult, especially obtaining spatial distributions of thickness.

Sample surface coating is an accepted method for improving the absorption of the pumping beam to the sample as well as radiation efficiencies from the sample; but so far simple and highly controllable methods of coating have not been presented. High resolution for metal film thickness measurements can be obtained with this method. Furthermore, we measured the thermal diffusivities of each thin metal film and analyzed the origin of the clear linear relationship between film thickness and measured photothermal detected signal amplitude.

2. Experimental Apparatus

Photothermal radiometry was used as a photothermal detection method. Figure 1 shows the block diagram of our experimental apparatus.[2] Here, a laser diode (maximum fiber-out power: 600 mW, wavelength: 810 nm) was used as the pumping laser. The light beam from the laser diode was introduced to an optical fiber having a collimator at the tip. The emitted infrared (IR) radiation from the sample was focused by using two parabolic IR reflection mirrors (focal length: 150 mm, Ultra Precision Tech. Co. Ltd.) on a 1 mm square HgCdTe photoconductive IR detector (Model J15D14, EG&G Judson Co. Ltd.). A germanium filter whose IR wavelength bandpass range is 2–12 μm was placed in front of the detector to eliminate the scattered pumping

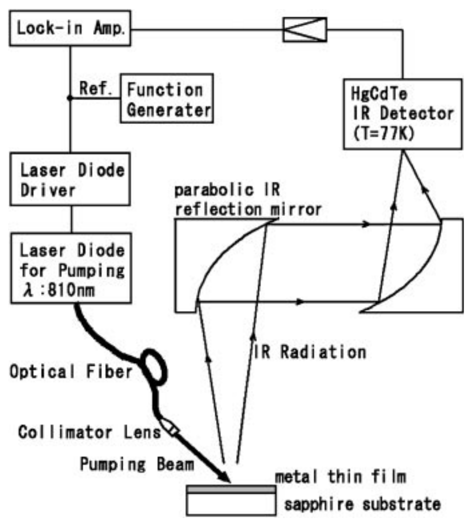

Fig. 1. Block diagram of experimental apparatus.

*E-mail address: s03dn01@sub.osaka-sandai.ac.jp

beam. The detected signal was fed to a lock in an amplifier and synchronously detected by modulation frequency.

3. Experiments and Results

3.1 Sample surface black coating

Sample surface black coating is a common method to improve absorption and the radiation efficiencies of the pumping beam. The controllability (reproducibility) of the paint thickness, however, is definitely important in sample surface black coating when used to measure delicate differences in certain quantities of various samples such as the film thickness of samples. Figure 2 explains this concept. If the paint is too thick, the photothermal signal value won't be determined by the metal thickness but by the paint thickness; on the other hand, if it is too thin, the paint won't function well as a pumping beam absorption material. Consequently, an "optimum paint thickness" must be located. Considering such factors and requirements for the simplicity and reproducibility of black coating, a spin-coating method (Spin coater: 1H-D2, MIKASA) was adopted. We used graphite (LODD RESEARCH, #60790) diluted with propanol as blackening paint. After many trials of spin coating with a different number of rotations, we determined that the optimum number of rotations for spin coating was 2000 rpm (30 s). When the graphite concentration ratio to propanol was too high, the graphite particles themselves damaged the metal film.

Figure 3 shows an example when graphite diluted with propanol at a 1:15 ratio was spin-coated on aluminum thin film. Figure 3(a) represents the surface view, and Fig. 3(b) represents the view from the surface when the sample was lighted from the back. Damage to the metal thin films is clearly seen. Based on these results, a very low dilution ratio of 1:100 was applied. The thickness of the black paint after only one spin coating, however, proved too thin at such a low dilution ratio. To compensate, multiple spin coatings were applied to obtain an appropriate thickness. Figure 4 shows the relationship between the detected infrared radiometric signal amplitude and the number of spin coatings. As a sample, 180 nm thick aluminum thin film formed by vacuum deposition on a sapphire substrate was used. Spreading was also verified by repeating the same experiment five times at every number from zero to ten spin coatings. As shown in the figure, the detection signal values almost linearly increased in proportion to the number of spin coatings, up to five times spin coatings. The signal values, however, almost reached saturation at over five spin coatings; the spreading of the signals increased, too. The reason can be explained as follows. When the number of coatings exceeds five, the adhesive force between the graphite layer formed by the five previous coatings and the graphite layers subsequently formed (more than five times) is weakened due to the continued accumulation of graphite, making it easier for the graphite to be irregularly scraped off by the graphite particles spin-coated afterwards. These experiments clarified that an "optimum paint thickness" can be obtained by applying 5 spin coatings.

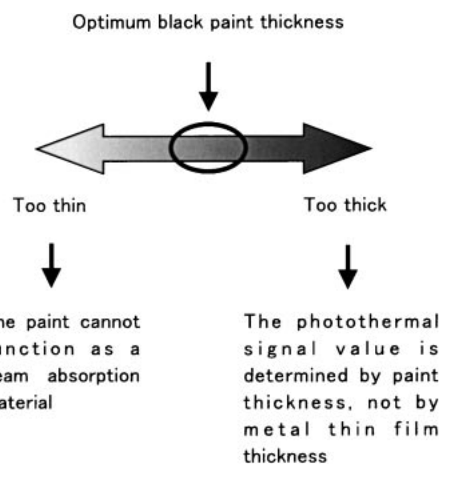

Fig. 2. Black coating concept.

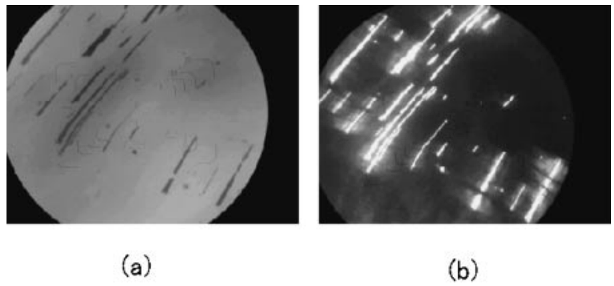

Fig. 3. Damage when graphite diluted with propanol at a 1:15 ratio was spin-coated on Al thin film (a) surface view, and (b) surface view when lighted from back.

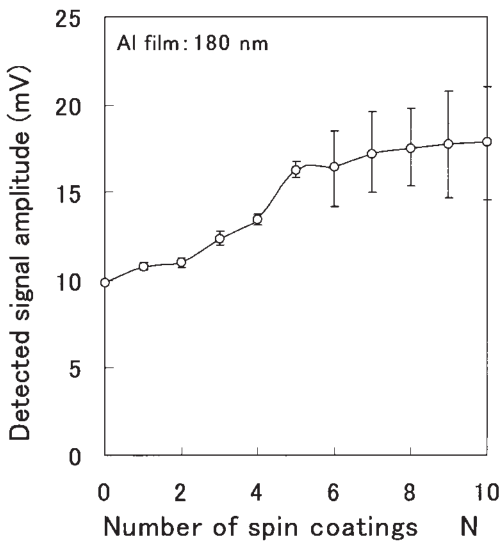

Fig. 4. Relationship between detected signal amplitude and number of spin coatings.

3.2 Relationship between detected signal amplitude and aluminum film thickness (black coating)

Figure 5 shows the relationship between the detected signal amplitude and the aluminum film thickness with and without five spin coatings of black paint. Here, the pumping beam modulation frequency is 10 Hz. Both lines show a clear linear relationship between detection signals to the aluminum film thickness. As shown in the figure, the inclination of the line showing the relationship between detection signals to the aluminum film thickness with black

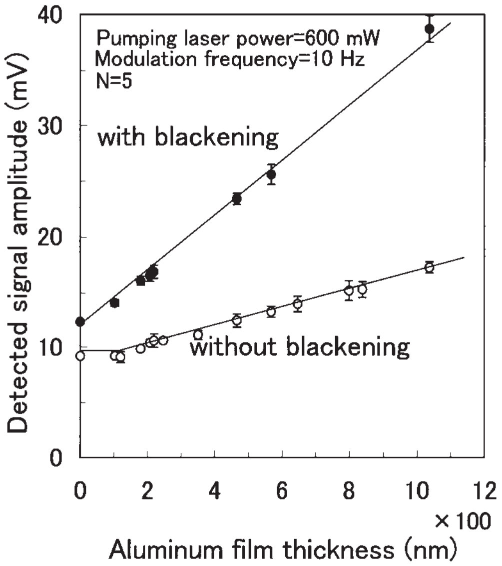

Fig. 5. Relationship between detected signal amplitude and aluminum film thickness (black coating).

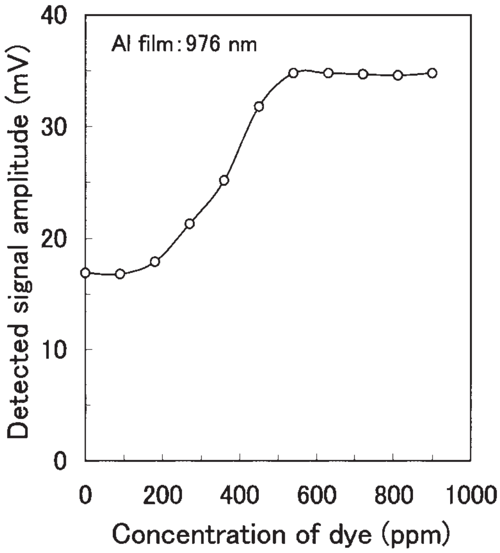

Fig. 6. Relationship between detected signal amplitude and concentration of dye.

coating is about 0.026 mV/nm in all the film thickness regions including 0 μm, while that without black coating is about 0.008 mV/nm in the film thickness regions over 100 μm. Comparing both inclinations reveals that the former measurement's sensitivity is more than three times larger than the latter. Besides, regarding the characteristics under/around the 100 nm thick region in the figure, the detection signal line without black coating shows flat characteristics, but the line with black coating shows linear inclination. Accordingly, the measurement of metal films whose thickness is less than 100 nm is possible with black coating and impossible without black coating. These results prove that our black coating method is extremely effective. They also show that such a black coating method can achieve resolution on the order of a few nm with a film thickness measurement.

3.3 *Sample surface dye coating*

Sample surface coating effectiveness was confirmed by the black coating results shown in the above paragraphs. The demerit of this black coating, however, is the difficulty of removing the coating material after the metal film thickness measurement. The difficulty, however, does not necessarily suggest a destructive inspection method, because the coating material does not damage the samples themselves. However, a new coating material was developed that aimed for a "perfect" nondestructive inspection.

As new coating material, photoresist has received attention because of the simplicity of its removal. The photoresist material applied is AZ1500, which can be easily removed by acetone. The pumping beam, however, is not absorbed into the photoresist but is absorbed into the dye mixed in the photoresist. That is, the wavelength of the photo absorption peak of the pumping beam is almost the same as the wavelength of the dye, but not the same as photoresist. Powdered IR-140 was used as the dye, which was first mixed with acetone. The solution of dye with acetone is successively mixed with photoresist, which was used as a new coating material. It was also coated on the metal film by a spin-coating method. The dye concentration limit that can be melted in acetone is 900 ppm.

The new coating material has the following three advantages over the blackening material: it is easily removable by acetone; one spin coating is enough for the coating because the solution does not damage the metal thin films; and the appropriate viscosity for coating is easily obtained by changing the ratio of acetone and photoresist.

It is also necessary to obtain the optimum conditions for the dye coating, as in the blackening method. Figure 6 shows the relationship between the detected infrared radiometric signal amplitude and the concentration of dye. As a sample, 976 nm thick aluminum thin film formed by vacuum deposition on a sapphire substrate was used. The detection signal was determined by the concentration of dye, not by the photoresist, because the wavelength of the pumping beam is quite different from the photo absorption peak of the photoresist. After many trials of spin coatings, the dilution ratio of dye into acetone and the optimum number of rotations for spin coating were determined to be 1:5 and 1500 rpm (30 s), respectively. As shown in the figure, the detection signal values almost linearly increased in proportion to the dye concentration. The signal values, however, almost reached saturation at over 560 ppm because, in the region where the dye concentration is comparatively low, the pumping beam energy is not all absorbed into dye coating; some reaches the metal thin-film surface and reflects it. In regions where the concentration of dye is comparatively high (560 ppm or more), the pumping beam energy doesn't reach the metal thin-film surface; all is absorbed in the dye. Consequently, the detection signal is saturated in the region where the concentration of dye is more than about 560 ppm, where the coating effect is almost equal. As a result, a 900 ppm concentration of dye was adopted in our experiment.

3.4 *Relationship between detected signal amplitude and aluminum film thickness (dye coating)*

Figure 7 shows the relationship between detected signal

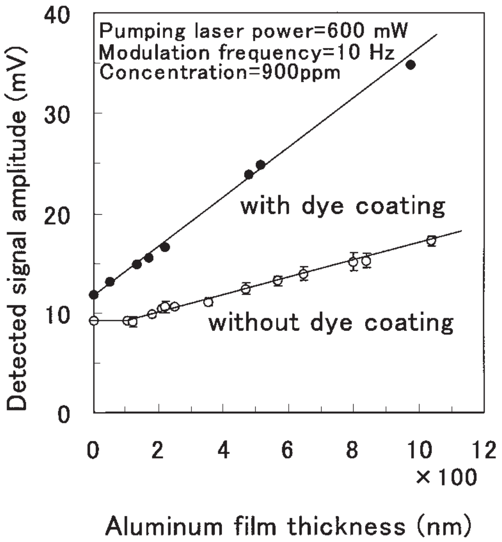

Fig. 7. Relationship between detected signal amplitude and aluminum film thickness (dye coating).

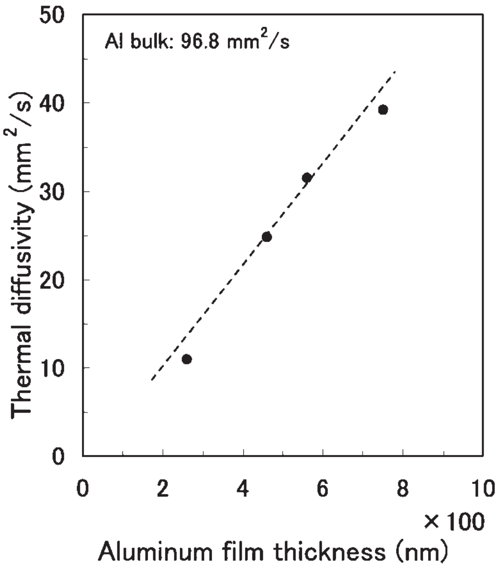

Fig. 8. Relationship between thermal diffusivity and aluminum film thickness.

amplitude and aluminum film thickness (dye coating). The experimental conditions are nearly the same as the blackening method. As shown in the figure, the inclination of the line showing the relationship between detection signals to aluminum film thickness with dye coating is about 0.024 mV/nm, while that without dye coating is about 0.008 mV/nm. Namely, the inclination of the detection signals to the aluminum film thickness with dye coating is about three times larger than without dye coating. As in the black coating case, based on characteristics under/around 100 nm of metal thickness in the figure, the same results for the possibility of film thickness measurement under/around 100 nm of metal thickness can be concluded. That is, excellent results similar to black coating were obtained.

This method is very simple for ultra thin-film metal thickness measurement with very high sensitivity. Here we investigated the relationship between measurement sensitivity and thermal diffusion length. The relationship between thermal diffusion length μ and the pumping beam modulation frequency is given by the following eq. (1),[3] where α is thermal diffusivity and f is pumping beam modulation frequency:

$$\mu = \sqrt{\frac{\alpha}{\pi f}} \tag{1}$$

This equation shows that if the frequency is too high, then the detection signal value is too low and vice versa. If the frequency is comparatively low, the detection signal value is high enough but the signal is influenced by both the metal film and the substrate. As already shown, the pumping beam modulation frequency of 10 Hz was adopted in our experiment. The thermal diffusion length, therefore, was calculated to be nearly 670 µm by using a thermal diffusivity value of sapphire substrate ($\alpha_{\text{sapphire}} = 14.1\,\mu\text{m}^2/\text{s}$). The value is more than 700 times bigger than the Al film thickness having the order of several hundred nm. Despite this fact, Figs. 5 and 7 show that our method achieved the order of a few nm film thickness measurement, illustrating the extreme effectiveness of our coating method.

3.5 Relationship between thermal diffusivity and aluminum film thickness

In the ultra-thin region of thin films, it is commonly known that thermal diffusivity changes depend on film thickness.[4] The thermal characteristics of the film are not necessarily equivalent to that of bulk, which is generally due to differences of qualities and/or the microstructures between the films and the bulk material. Therefore, the thermal diffusivities of the samples of every aluminum film thickness were measured to clarify the metal quality and/or the microstructure, as has often been performed elsewhere.[4] At the same time, our experiment also examined the origin of the clear linear relationships between detection signals and the thickness of aluminum film. A zero crossing method of photothermal mirage detection was utilized for the measurements whose results are shown in Fig. 8.[5] This figure shows that the thermal diffusivity value of all thin films is lower than the bulk material (96.8 mm^2/s), suggesting that the thermal characteristics of thin-film metal are different from bulk material. A clear linear relationship between detection signals and thermal diffusivity illustrates that a similar relationship between detection signals and aluminum film thickness, as shown in Fig. 8, more or less relates to the thermal diffusivities of the samples.

4. Conclusion

For the ultra thin-film metal thickness measurement by photothermal infrared radiometric detection method, a sample surface coating method was proven quite effective to improve measurement sensitivity. The sensitivity ratio with and without sample surface coatings was about three for both black and dye coatings. By applying our sample surface coatings method, the measurement of film thickness of even less than 100 nm (~0 nm) is quite possible with a resolution measurement of a few nm. Among black and dye coating methods, the latter is simpler and less nondestructive than the former. Our experiments also clarified that a clear linear relationship between detection signals to the aluminum film thickness more or less relates to the thermal diffusivity of each sample. Our method has the following advantages: it is obtainable even if the quality of the film is uneven for various thicknesses; the thickness is obtainable without any material constants of films; and not only the average film thickness but also its special distributions are measurable by selecting the pumping beam radii.

The effectiveness shown above functions for the other photothermal measurements. This method is considered the most easily introducible to industrial fields.

1) M. B. Suddendorf, M. Liu and M. G. Somekh: Appl. Phys. Lett. **62** (1993) 3256.
2) A. Yarai, Y. Okamoto and T. Nakanishi: Rev. Sci. Instrum. **74** (2003) 652.
3) A. C. R. da Costa and A. F. Siqueira: J. Appl. Phys. **80** (1996) 5579.
4) J. Jauregui, Z. L. Wu, D. Schafer and E. Matthias: *Proc. 7th Int. topical meeting Photoacoustic and Photorhermal Phenomena, Doorwerth, Netherlands, 1991* (Springer-Verlag, Berlin, 1992) p. 682.
5) P. K. Kuo, E. D. Sendler, L. D. Favro and R. L. Thomas: Can. J. Phys. **64** (1986) 1168.