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LASER-INDUCED SURFACE ACOUSTIC WAVES FOR THIN FILM CHARACTERIZATION

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Abstract. Knowledge of mechanical properties of thin films is essential for most of their applications. However, their determination can be problematic for very thin films. LAW (Laser-induced acoustic waves) is a combined acousto-optic method capable of measuring films with thickness from few nanometers. It utilizes ultrasound surface waves which are excited via short laser pulses and detected by a PVDF foil. Properties such as Young's modulus, Poisson's ratio and density of both the film and the substrate as well as film thickness can be explored.Results from the LAW method are successfully compared with nanoindentation for Young's modulus evaluation and with optical method for film thickness evaluation and also with literature data. Application of LAW for anisotropy mapping of materials with cubic crystallographic lattice is also demonstrated.

Keywords: Anisotropy, laser-induced surface acoustic waves, nanoindentation, thin films, Young's modulus.

1. Introduction

Thin films and coatings have become an essential part of our everyday lives and knowledge of their mechanical properties and durability directly affects their lifetime regardless of their primary role. Thin films are often exposed to external stresses during their fabrication or service life. Therefore, their reliable testing is essential for both their research and development as well as industrial production.

Nanoindentation has become the standard method for determination of local mechanical properties, but it has its inherent limitations [1]. Mostly the thickness of the film is the main limiting factor, because if the indenter penetrates to a greater depth than 10 % of the film (commonly used rule of thumb), then substrate may affect the hardness values considerably [2–4]. Determining the elastic modulus of very thin films is even more problematic because the substrate and the film behave like two springs in series hence the elastic modulus of the film is always affected by the substrate [5]. This means that the indentation of films with thickness under 50 nm is very challenging [6].

However, mechanical properties of very thin films can still be explored using the methods based on analysis of the dispersion curves of Rayleigh surface acoustic waves. One of such methods is the LAW (Laser-induced Acoustic Wave) technique [7, 8]. It is a combined acousto-optic method developed for the assessment of material characteristics of surfaces (Young's modulus, Poisson's ratio, density, film thickness) based on the generation of surface acoustic waves and their detection. The propagation of these waves in the material depends on the elastic properties of both the thin film and the substrate.

In order to demonstrate the possibilities and strengths of the LAW, the representative results from thin films and single crystals are presented. In case of thin films the results are compared with the results from other methods such as nanoindentation for Young's modulus evaluation or optical methods for film thickness characterization. Besides, the limit of the film thickness is explored, as the ability to characterize very thin films is one of the main advantages of LAW over other methods.

1.1. Principle of LAW

Short laser pulses from nitrogen laser are absorbed by the material and cause generation of a wide frequency spectrum (typically in the range from units to hundreds of MHz) of thermally activated surface acoustic waves (SAW). Those waves are propagating from the point of incidence and mostly in the surface layers of the sample as their amplitude decays exponentially with the increase of the distance from the surface [7] as shown in the Figure 1.

The penetration depth h_{pen} of the SAW can be estimated by their wavelength ($h_{\text{pen}} \approx \lambda$). This

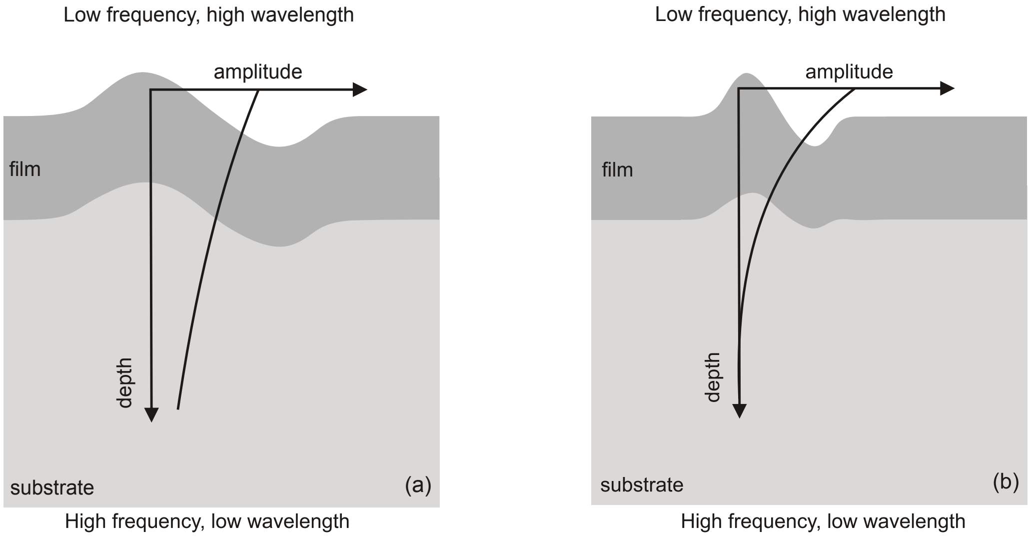

Figure 1. Propagation and amplitude-decay of SAW with a) low frequency and b) high frequency

means that the penetration depth depends on the frequency $f(\lambda = v/f\ )$. The greater the frequency the lower the penetration depth. Because most of the wave energy is concentrated on the surface, SAW are very sensitive to very thin films with thicknesses from few nanometers (even when they are much thinner than the penetration depth of SAW) [8].

The phase velocity v of SAW in a non-coated homogeneous and isotropic material is independent on frequency and can be described as:

$$\nu = \frac{0.87 + 1.12\nu}{1+\nu}\sqrt{\frac{E}{2\rho(1+\nu)}}, \tag{1}$$

where ν is Poisson's ratio, ρ is material density and E is Young's modulus. This means that phase velocity is directly linked to the elastic modulus, Poisson's ratio and density of the material. However, situation is different in coated materials, where the penetration depth depends on frequency so the phase velocity of the SAW must as well. This phenomenon is called the dispersion. In case of a substrate with low phase velocity coated with a thin film with a high phase velocity, then the phase velocity for the film/substrate system increases with frequency.

For explanation let's assume infinite substrate and SAW propagating across the surface. Theoretically for the wave with frequency approaching zero, the penetration depth would be approaching infinity. That in turn means that the contribution from the thin film would be negligible. On the contrary, if the SAW would have infinitively high frequency, then the wave would be restricted only to the very top of the sample, in other words the wave would propagate only in the film according to the eq. (1).

The precise relation between the frequency f and phase velocity v of the SAW on coated materials depends on elastic properties and densities of both the substrate and the thin film as well as on the thickness of the film. This means that if the dispersion curve and some of the variables are known, the rest of them can be calculated.

In order to get the dispersion curve the SAW must be detected in various known distances from the point of incidence using a PVDF foil which transforms the mechanical vibrations into electric signal, see principal scheme of LAW method (instrument) in Figure 2. The dispersion curve is then calculated using the following equation:

$$\nu(f) = \frac{2\pi f\,(x_2 - x_1)}{\phi_2(f) - \phi_1(f)}, \tag{2}$$

where x_1 and x_2 are two different distances between the sensor and the point of incidence, $\phi_1(f)$ and $\phi_2(f)$ are the phase values of the surface wave frequency f. The whole experimental set-up can be seen in Figure 2.

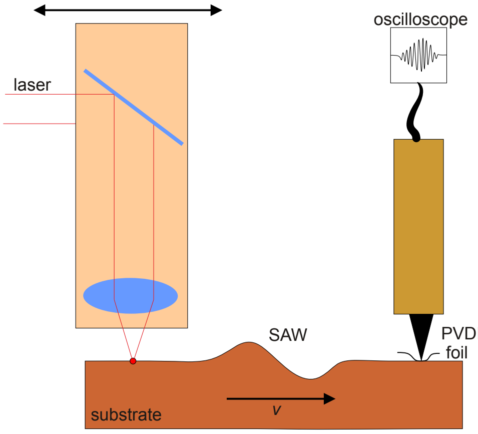

Figure 2. Schematic representation of the LAW set-up.

1.2. Experimental details

The experiments were performed on a Laser acoustic test system LAwave (Fraunhofer institute, Dresden, Germany). Acoustic waves with frequency ranging from ∼ 1 MHz up to ∼ 250 MHz were generated using a 337 nm N_2 laser with a 0.5 ns pulse duration and

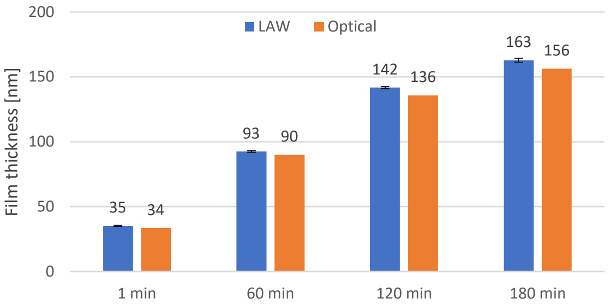

Figure 3. Film thickness of samples from dry thermal growth measured by LAW compared to results from optical method.

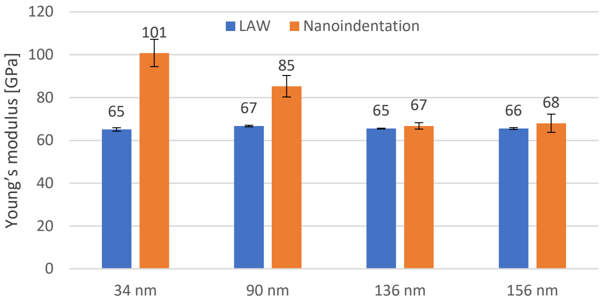

Figure 4. Young's modulus of SiO_2 thin films with different thickness measured by LAW and nanoindentation.

400 µJ pulse energy. The signal from the PVDF foil was averaged from 64 measurements for each of the 5-7 measuring points along the 15 mm and 20 mm measuring path for glass and silicon substrates respectively. All measurements were done at a room temperature.

2. Results and discussion

2.1. Thin film characterization – Film thickness evaluation

Silicon dioxide thin films on Si(100) were used for the film thickness characterization. It is well known that high quality SiO_2 films are prepared by dry thermal growth which is considerably slower than for example wet thermal growth but yields high quality films – the oxide film is more uniform and its density is higher. This allows for more precise and reliable comparison of LAW and other methods as these SiO_2 films represent an ideal model system. The Si substrates were oxidized at 1000 °C in quartz tube for 1, 60, 120 and 180 minutes, the heating rate was 20 °C/min. The resulting film thickness can be seen in Figure 3. The optical reference measurement of the film thickness was performed on spectral reflectometer calibrated on polished silicon wafer with known profile of spectral reflectance.

Results from both methods are similar with the results from LAW being slightly higher in all cases. The highest percentage difference (4.6%) is for the thinnest sample. The standard deviation for LAW is very small. Thus, it may be concluded that LAW gives reasonable results for film thickness if Young's modulus and density are uniform and known. The native SiO_2 oxide layer (grown at room temperature) was measured as well in order to find out how accurate can LAW be for very thin films. Its thickness, when kept in dry pure oxygen, is around $\sim$1 nm [9], but thickness around 1.5-2.5 nm can be expected when exposed to air depending on the temperature and humidity with 2.1 nm given in [9]. Since LAW is very sensitive to the top surface conditions as well as presence of (sub)-surface flaws [10] and any structural imperfections, different Si(100) wafers of the same type and doping were explored (University Wafer, USA). This was confirmed by a strong variance in measured thickness of native SiO_2 film between different wafers. The native SiO_2 thickness of (3.2 ± 0.5) nm was obtained after the exclusion of the most extreme values that might be among others related to the sub-surface damage. These values are slightly higher in comparison with the literature data. This overestimation might be caused by the silicon suboxide interface layer formed between the Si and SiO_2, with thickness estimated to be $\sim$0.35 nm [11]. The interface behaves like a second thin film and might increase the resulting film thickness since in our fit only single film system with characteristics of SiO_2 is assumed. This means that even few nm thick films may be explored via LAW method provided the dispersion caused by the film can be easily seen and substrate of superb quality, with no surface and sub-surface damage, is used and effects of interface layers are included in the calculation.

2.2. Thin film characterization – Young's modulus evaluation

In order to explore the inherent limits of depth sensing indentation and LAW the SiO_2 films with different thicknesses were measured by both methods. The high quality SiO_2 films with thickness ranging from 34 to 156 nm grown on Si(100) mentioned in previous chapter were used. Nanoindentation experiments were performed using the fully calibrated NanoTest instrument equipped with a brand new Berkovich indenter. At least 15 measurements for each film were analyzed by standard Oliver-Pharr method. The indentation modulus E values were calculated using SiO_2 Poisson's ratio of 0.17 and considering the correction for diamond elastic deformation (Poisson's ratio of 0.07 and Young's modulus of 1141 GPa). It should be noted that indentation modulus can be considered as Young's modulus as long as pile-up and sink-in effects are absent [12]. Comparison of the results can be seen in Figure 4.

Figure 4 shows that the values obtained from LAW and nanoindentation are similar for the 156 nm and 136 nm thick films because nanoindentation was not strongly affected by the substrate. However, for the 90 nm film the indenter penetrated up to 25 % of

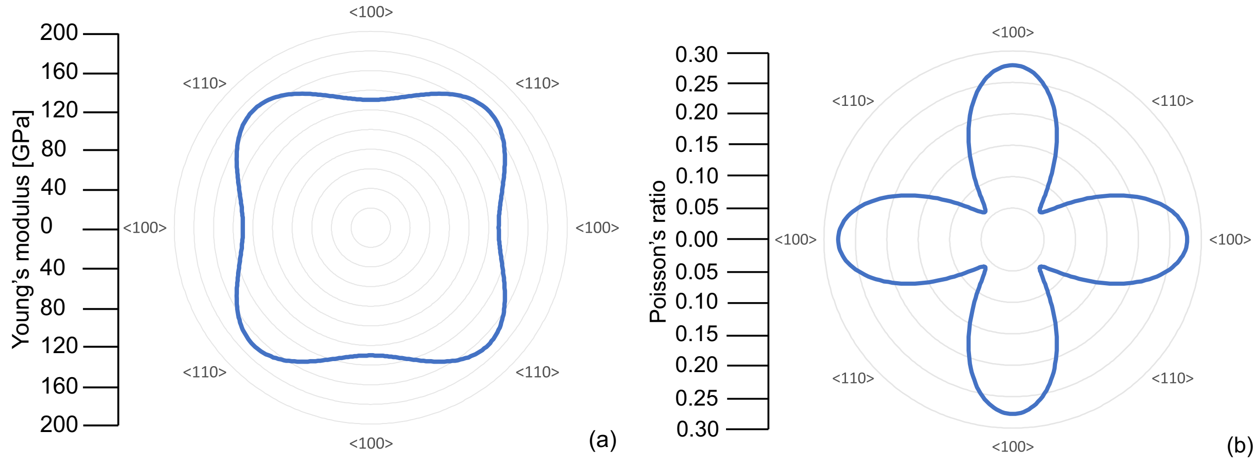

FIGURE 5. Si(100) anisotropy (a) Young's modulus (b) Poisson's ratio.

the film and the results are strongly affected by the substrate which has higher Young's modulus than the film. The 34 nm thick film shows even stronger substrate effect as 59 % of the film was penetrated and the resulting value of Young's modulus is somewhere in the middle between the value of the film and the value of the substrate. This clearly shows the unambiguous advantage of the LAW as the results obtained from LAW are constant despite the changing film thickness as opposed to nanoindentation. This is crucial for the characterization of very thin films. LAW can be affected by the film thickness as well, but only in the case of much thinner films as shown in the previous chapter reporting on characterization of native SiO_2 layer of ~2 nm thickness. Comparison in Figure 4 shows that the elastic modulus values obtained by nanoindentation are almost identical to those measured by LAW as long as the film thickness is high enough. In this case for the films thinner than 100 nm the unavoidable substrate effect leads to overestimation of the elastic modulus. For such thin films LAW can be viable alternative.

In order to present the robustness and universal use of LAW other films were also explored. Young's modulus was evaluated for aluminum film on glass, and titanium and chromium on silicon. The thickness of all three films was around 100 nm. Values obtained by LAW are compared with the values given by other authors [13–17] and in case of Al and Ti also with the results from nanoindentation. Table 1 shows that, the values of Young's modulus obtained by LAW correspond to those obtained from nanoindentation and are within the range reported in literature.

2.3. SILICON ANISOTROPY MAPPING

Single-crystal silicon is a well-known material with interesting properties and wide range of applications [18] that exhibits a strong anisotropy. Therefore, it is an ideal object for testing the LAW ability to explore material anisotropy.

Material	**Young's modulus (GPa)**		
	LAW	Reference	Indentation
Al	63.5	55-81	69.6
Ti	116.1	102-123	111.5
Cr	204.4	185-215	–

TABLE 1. Comparison of Young's modulus values of Al, Ti, Cr thin film measured by LAW, nanoindentation and literature data

In general, elastic behavior of cubic crystals may be fully described by three elastic stiffness constants C_{11}, C_{12} and C_{44} (for silicon at room temperature $C_{11} = 165.6$–165.7, $C_{12} = 63.9$, $C_{44} = 79.5$–79.6 GPa [18, 19]). Young's modulus and Poisson's ratio can be calculated in any direction from those constants. For example, Si(100) has Young's modulus ranging from 130.2 to 168.9 GPa [20], the minimal value is for the [100] direction and can be calculated as:

$$E_{[100]} = C_{11} - 2\frac{C_{12}}{C_{11} + C_{12}}C_{12}. \tag{3}$$

In this work, the elastic stiffness constants were measured in various directions on several Si (100) wafers. The resulting average values were $C_{11} = 165.4$, $C_{12} = 63.5$ and $C_{44} = 79.6$ GPa that is in excellent agreement with literature values listed above. Using these constant it is possible to plot a polar dependence of Young's modulus and Poisson's ratio. Figure 5 clearly shows the strong anisotropy of silicon elastic constants. Using LAW, anisotropy of any cubic crystals can be explored and elastic constants can be calculated for any other plane orientations.

3. CONCLUSIONS

LAW is a combined acousto-optic method developed for assessment of material characteristics of surfaces and can be used to obtain values of Young's modulus, Poisson's ratio and density for both the film as well as the substrate. It can also be used to obtain the values of elastic stiffness constants for anisotropic materials with cubic symmetry.

Films' thicknesses measured via LAW are very close to those from optical thickness measurements if input parameters are precisely known. Young's modulus measurements by LAW and by nanoindentation yielded same results for films with thickness over 100 nm, however as the indentation depth / film thickness ratio increased the data from nanoindentation started to be affected by substrate as the predicted by the commonly used 10 % rule of thumb (indenter should not penetrate deeper than to the 10 % of the film).

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