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Mechanical characterization of porous nano-thin films by use of atomic force acoustic microscopy

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ABSTRACT

The indentation modulus of thin films of porous organosilicate glass with a nominal porosity content of 30% and thicknesses of 350 nm, 200 nm, and 46 nm is determined with help of atomic force acoustic microscopy (AFAM). This scanning probe microscopy based technique provides the highest possible depth resolution. The values of the indentation modulus obtained for the 350 nm and 200 nm thin films were respectively 6.3 GPa ± 0.2 GPa and 7.2 GPa ± 0.2 GPa and free of the substrate influence. The sample with the thickness of 46 nm was tested in four independent measurement sets. Cantilevers with two different tip radii of about 150 nm and less than 50 nm were applied in different force ranges to obtain a result for the indentation modulus that was free of the substrate influence. A detailed data analysis yielded value of 8.3 GPa ± 0.4 GPa for the thinnest film.

The values of the indentation modulus obtained for the thin films of porous organosilicate glasses increased with the decreasing film thickness. The stiffening observed for the porous films could be explained by evolution of the pore topology as a function of the film thickness. To ensure that our results were free of the substrate influence, we analyzed the ratio of the sample deformation as well as the tip radius to the film thickness. The results obtained for the substrate parameter were compared for all the measurement series and showed, which ones could be declared as free of the substrate influence.

1. Introduction

The integration of new materials into novel microelectronic products is always challenging. Particularly, porous organosilicate glass used as insulating dielectrics in on-chip interconnect stacks must meet a complex set of materials properties including dielectric permittivity and Young's modulus. The incorporation of CH_2- and CH_3-groups and pores into silica networks significantly reduces the values for Young's modulus and hardness of the thin film material [1]. However, the mechanical properties of the so-called ultra-low k (ULK) materials can be improved by adjusting the pore concentration, as well as their shape, size, and arrangement, referred to as pore topology. The stability of the pore topology across the film thickness becomes yet another factor that needs to be characterized as the miniaturization tendencies progress in the nano-electronics industry.

Brillouin light scattering, surface acoustic wave spectroscopy [2], picosecond ultrasonic methods [3], and ellipsometric porosimetry [4] methods have been used to determine the values of Young's modulus of very thin films. The values obtained are free of the substrate influence and represent the mean value integrated from a relatively large area. One can use contact methods such as nanoindentation [5] and methods based on atomic force microscopy (AFM) [6] to determine mechanical properties from a confined region. The exact diameter of the contact area is defined by the contact mechanics models and may vary from few tens of nm to few hundreds of nm depending on the elastic properties of the indenter and the sample, indenter's geometry and the load applied to maintain the contact between the bodies.

State of the art nanoindentation instruments are capable of performing indentations with depth of 20 nm and less. To determine the indentation modulus of a thin film without considering the influence of the substrate, the indentation depth must be significantly less than the film thickness. Furthermore, as soon as the film thickness becomes less than 1 μm, additional factors have to be taken into account, for example the relative difference

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in the elastic properties of the film and the substrate as well as the ratios of the contact radius and indentation depth to the film thickness [5,7].

Small indentation depth experiments are not trivial [8] and in case of very thin films they do not always guarantee a result independent on the substrate properties. Thus, numerous models accounting for substrate influence on the load–displacement (P–h) curves measured on thin-film samples in nanoindentation experiments have been developed during the previous 30 years. Doerner and Nix [9] proposed a method for the determination of Young's modulus from the initial part of a standard load–displacement curve measured in nanoindentation. Their empirical model took into account the ratio between the film thickness and the effective indentation depth. Their expression also included constants that had to be determined empirically from P–h curves measured on a thin film sample as well as on a bulk substrate. The model proposed by King [10] took into account the influence of the tip geometry on the measured P–h curve. His results showed that the effective elastic properties of the film–substrate system depended on the contact radius to film thickness ratio a/t. Moreover, he determined the values of the geometry factor for flat punches of different geometries (circular, triangular and square) as a function of the a/t ratio. A closed form solution for the contact compliance of a film–substrate system was proposed by Gao [11]. The so-called perturbation analysis is based on the known elastic solutions for a reference homogenous body made either of the film or the substrate material. The particular elastic properties of the reference homogenous material determine the limits of the perturbation solution. However, Gao's approach is valid only for film–substrate system with a maximum relative difference in their elastic properties of about 200–300%. In the cases, where the substrate is much stiffer than the film, Swain and Mencik [12] adapted a model developed for large-scale indentation of rubber sheets published by Waters [13].

The models proposed in [9–11,13,14] can be expressed in a general form:

$$\frac{1}{M_{eff}} = \frac{1}{M_s}[1 - f(t, a, h, \alpha)] + \frac{1}{M_f} f(t, a, h, \alpha), \quad (1)$$

The effective indentation modulus M_{eff} is the modulus of the film–substrate system determined at given load conditions, M_s is the indentation modulus of the substrate, and M_f is the indentation modulus of the film. The function $f(t, a, h, \alpha)$ describes how the substrate properties affect the effective indentation modulus of the system as a function of the film thickness t, contact radius a or indentation depth h and a parameter α that is related to the tip geometry.

The determination of the mechanical properties of thin films from the unload part of the P–h curve obtained in the plastic–elastic regime is limited due to possible film cracking and delamination, reverse plasticity, creep, or viscoplasticity. A method developed and tested by Schwarzer and Chudoba [15–17] allows characterization of very thin films (in nm range) from the analysis of elastic interaction between a relatively large spherical indenter (from few to several μm in radius) and a film–substrate system. Their method is based on an analytical stress–strain solution of a contact problem for a layered half-space system under defined load conditions and calculating the resulting surface displacement. Those are then compared to the displacement measured in the experiment. The main advantage of this method is that it allows for application of relatively large loads that can be maintained with high precision by a nanoindenter. However, the stability of the measurement in the elastic regime is paid by a loss of the lateral resolution.

Another approach was proposed by Li and Vlassak in [18]. They implemented Yu's elastic solution into an analysis procedure that allowed for the estimation of the contact area from the P–h curve obtained on a thin film sample in a range of the indentation depth that could be easily maintained by the instrument. Li's method allows for large mismatch in the mechanical properties of the film and the substrate. Bull [19] proposed a very simplified approach to evaluate the modulus of a film–substrate system where no empirical geometry factors are needed. However, this model has also problems for systems with large differences in Young's moduli of the film and the substrate.

Methods based on atomic force microscopy (AFM) [6] offer the ability to control the static loads in the range of single nN and exert localized pressures with very sharp tips with radii below 20 nm yielding unparalleled spatial resolution for contact probing. AFM-based methods can be used to obtain color-coded maps of such quantities as tip–sample adhesion, Young's modulus, storage and loss moduli, and indentation modulus [20–27]. There are several methodologies utilizing AFM instruments for mechanical characterization of materials. The most direct way to study mechanical properties of a sample is to record the force–displacement curves and interpret them in terms of contact mechanics [28]. The force–displacement curve can be measured during the standard approach of the cantilever to the sample surface at each point of the image (force volume method) [28], or by monitoring the cantilever deflection as the z-offset of the piezotube is modulated at frequencies below the first natural frequency of the cantilever (Pulsed-force mode) [29]. In addition, the analysis of the cantilever vibrations at its flexural and torsional modes is used to recalculate the calibrated force–displacement curves in the so-called torsional harmonic cantilever mode [20].

The AFM methods based on force–distance measurements are most effective when applied to compliant materials such as biological tissue or polymer. To access the information on the mechanical properties of materials such as glasses, metals and ceramics one must restore to dynamic modes of AFM operation. The term “dynamic” relates to vibrations of the AFM cantilever at frequencies greater than that of the first free flexural mode. Dynamic modes encompass several methods such ultrasonic force microscopy (UFM) [30], ultrasonic atomic force microscopy (UAFM) [31], and atomic force acoustic microscopy (AFAM) [32] that was further developed into contact-resonance force microscopy (CR-FM, and CR-AFM) imaging methods [33,34].

There are several publications reporting successful applications of the AFAM methods in the field of thin film characterization. For example, the indentation modulus of niobium films with thicknesses below 300 nm was determined in single point measurements [35], as well as from stiffness maps [36] obtained by use of AFAM and CR-FM methods, respectively. Stan and Cook [34] successfully characterized 100 nm thin films of granular gold with CR-AFM. Indentation moduli determined for 800 nm, 200 nm, and 50 nm thin films of nanocrystalline nickel showed the influence of the increasing intercrystalline volume on the effective elastic properties of the sample [37]. In these studies, the investigated films were thick enough to allow their direct characterization and to neglect the influence of the substrate.

AFAM and similar methods were also used to characterize mechanical properties of films thinner than 50 nm. Hurley et al. used the CR-FM method to study the adhesion at an interface of a 20 nm thin film of gold and silicon substrate [38]. Muraoka applied cantilevers modified with point weights to characterize 10 nm thin diamond-like-carbon layers by use of the AFAM method [39]. The AFAM method was also used to determine the indentation modulus of silicon oxide films with thicknesses ranging from 8 nm to 28 nm [40]. In the studies presented in [39,40] the substrate influence was considered. The results presented in this paper were obtained by combining the ability of the AFAM method to