Testing Thin Films Surfaces

The Laser-acoustic Technique LAwave

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One of the most important topics within the field of nanotechnology is the fabrication of nanoscaled coatings and their applications in different branches. The spectrum ranges from the utilization of ultraprecise nanoscaled multilayers in x-ray optics to protective coatings in hard disk drives which only have a thickness of a few nanometers. The semiconductor industry in particular has developed highly sophisticated methods for the production of different precise coatings which are a prerequisite for the manufacture of modern electronic devices.

It is mandatory that this progress in manufacturing methods has to be accompanied by the development of adequate and sensitive characterization methods. A technique that advantageously can complete the established mechanical micro- and nano-testing methods is the laser-acoustic technique LAwave based on surface acoustic waves. This method is very sensitive to micro-structural variations near the surface.

In addition, by using high frequencies surface acoustic waves can sense coatings with a thickness of only a few nanometers. Moreover, this method allows for fast and non-destructive testing. Three examples are presented illustrating how this technique can be advantageously applied for measuring properties in the nanometer range: testing top coatings for computer hard disks, evaluating mechanical properties of high-porous low-k films and analyzing subsurface damage in cup-grinded silicon wafers.

Apart from chemical and topographic analyses, interest is focused on the mechanical characterization of materials used in nano-components. For the complex structures of micro- and nano-products, optimizing and matching the mechanical material properties is very important to guarantee the reliability of micro- and nano-products.

Most of the fabricated micro- and nano-structures contain materials other than that of the substrate, which are obtained by various deposition techniques, or by modification of the substrate. The exact knowledge of the material properties, as elastic modulus, hardness, expansion coefficient, fracture toughness, is absolutely necessary for optimizing the thermo-mechanical response of micro- and nano-devices.

For the viewpoint of characterization, nano-scale science and technology are strongly driven by *scanning probe microscopy* (SPM) which allows investigation and manipulation of surfaces down to atomic scale [1]. The SPM techniques enable imaging the surface with a resolution in the atomic range and to evaluate important topographic and tribological parameters, as elastic response, hardness or scratch resistance. Another widely used technique for local mechanical testing in the micro-range is the depth sensing nano-indentation tester, an advance of the classical hardness tester making an imprint in the test material by a loaded diamond tip. The nano-indentation enables hardness and elastic modulus of material region in the sub-micrometer range to be determined.

The laser-acoustic device LAwave has proved an interesting test technique to complete and extend the possibilities of the mechanical surface analyzing methods. It is an ultrasonic technique making use of the dispersion of surface acoustic waves. This acoustic wave mode is very sensitive to surface modification also in the depth of nanometers. The LAwave device measures the dispersion spectrum, also termed dispersion curve, and calculates the material parameters of the film material by fitting a dispersion curve deduced from a theory of surface acoustic wave dispersion. Advantages of the technique are that it can yield fast and reliable results without special sample preparation. The test is non-destructive and can be applied to film materials with a wide range of properties, from soft as polymers to hard as diamonds. On silicon, films down to a few nanometers film thickness can be investigated. For the metallurgical coatings, the thickness can reach up to some hundred micro-meters.

Compared to the SPM and indentation tester, the technique has a poor lateral resolution. The spot of the measurement is 3 mm × 10 mm. It senses nano-dimensions in direction perpendicularly to the surface.

The LAwave Technique

Surface acoustic waves are elastic vibration with amplitude in the range of nanometers propagating along the surface of the material. The amplitude is highest at the surface and decays within the material exponentially. At a depth corresponding to the wavelength, the amplitude is decayed to 1/e of the oscillation at the surface. This distance to the surface is defined as the penetration depth of the surface acoustic wave. The penetration depth reduces with increasing frequency. The higher the frequency, the more the film influences the wave propagation. Due to the exponential decay of the amplitude, the wave energy is concen-

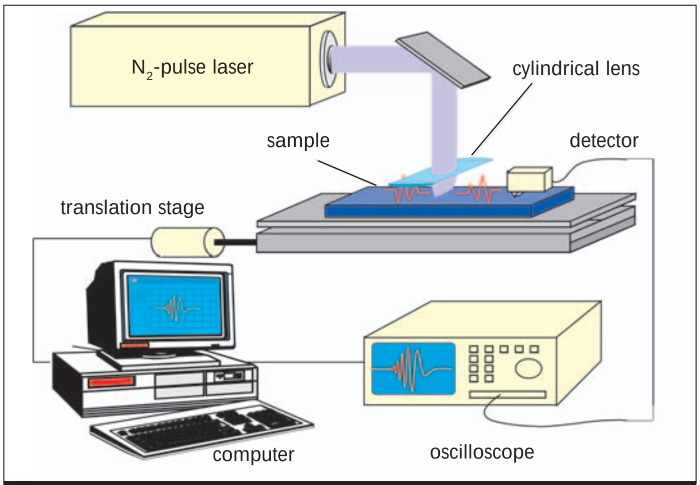

Figure 1: Schematic representation of the laser-acoustic device LAwave. The technique uses short pulses of a nitrogen laser focused into a line that create wide-band surface acoustic waves which are detected by piezoelectric transducer.

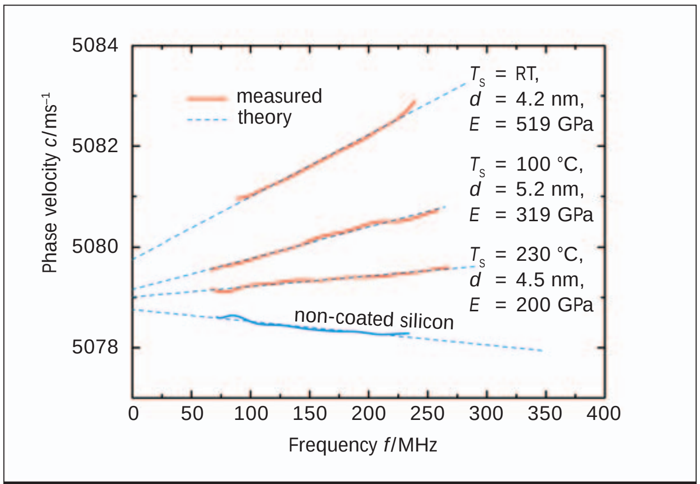

Figure 2: Dispersion curve for nanometer ta-C-films on silicon deposited by Pulsed High-Current Arc. The results reveal that deposition at room temperature produces films with the highest Young's modulus.

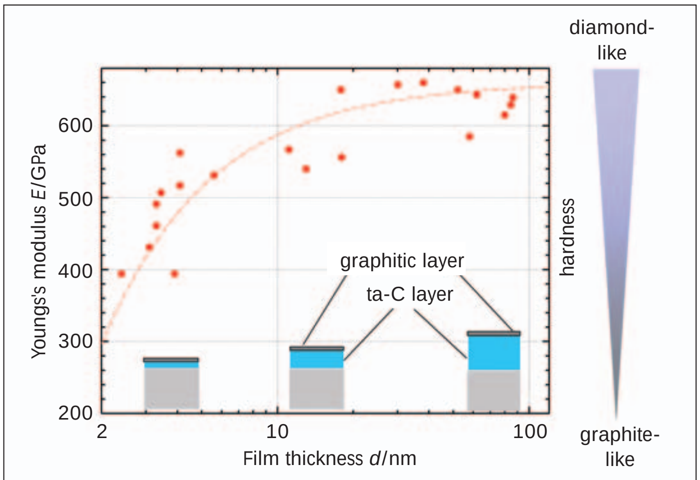

Figure 3: Young's modulus E depending on film thickness δ for ta-C-films deposited with Pulsed High-Current Arc. The film property is nearly constant in the range above 20 nm.

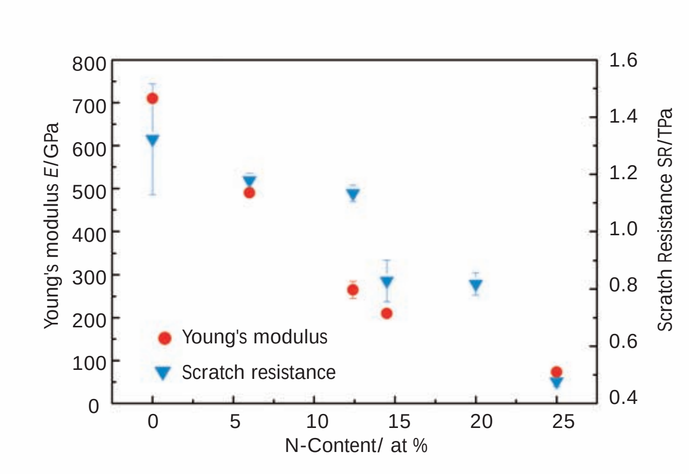

Figure 4: Correlation between Young's modulus E and scratch resistance SR for nanometer carbon films with increasing nitrogen content. The scratch resistance has been measured by atomic force microscope equipped with a diamond cantilever [8].

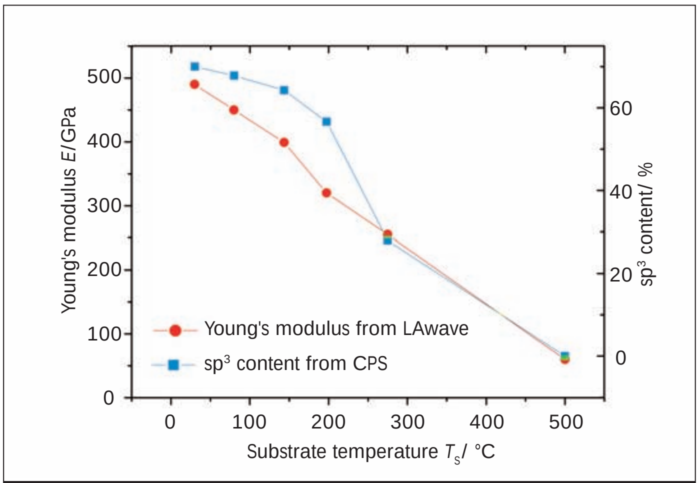

Figure 5: Correlation between Young's modulus E and content of sp^3-bonds for ta-C-films [9]. The fraction of sp^3-bonds has been measured by X-ray photo-electron spectroscopy (XPS). The bonding condition has been varied by depositing the films at different substrate temperature T_S.

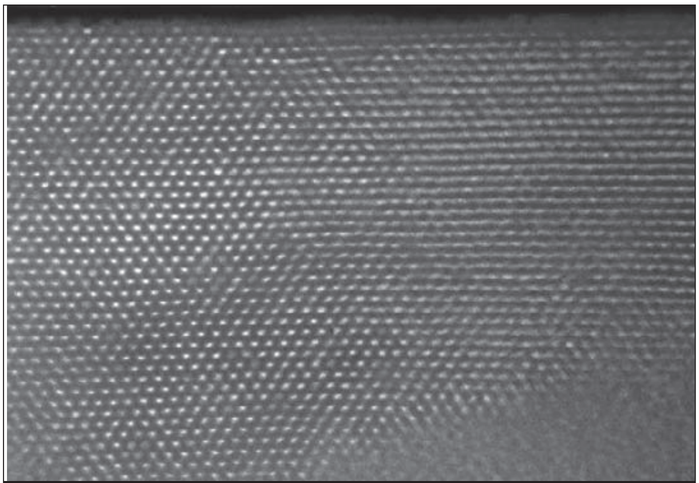

Figure 6: Nano-porous low-k films with porosity higher than 40 % (Fig. 6) have promising dielectric properties with a permittivity of $\kappa < 2.3$ [10].

trated at the surface, making the wave propagation very sensitive to thin films and micro-structural gradients beneath the surface. This is the reason that films to be tested can be much thinner than the penetration depth of the wave. Whereas for a completely homogeneous sample, the wave velocity is constant, a film with a thickness less than a few percent of the penetration depth of the wave causes the propagation velocity of the wave to depend on frequency. This phenomenon is termed dispersion. The LAwave technique measures the spectrum of the wave velocity in the range of 200 MHz, termed dispersion curve. The dispersion can be modeled by a theory containing the material parameters involved, elastic constants and density of film and substrate, and the film thickness as well [2]. The LAwave device fits the theoretical curve to a dispersion curve measured to yield the interesting material parameters.

In order to measure the dispersion curve, the LAwave technique uses short pulses of a nitrogen laser focused into a line that create wide-band surface acoustic waves which are detected by piezoelectric transducer (Fig. 1) The transducer transforms the mechanical waveform into an electrical signal [3]. Signals are detected at different distances between the laser focus line and the transducer. They are recorded by an oscilloscope and Fourier-transformed, yielding the amplitude and the phase spectra of the waveforms. With the phase spectra of the waveforms, the phase velocity can be calculated for all frequencies included in the waveform spectrum. This signal processing yields the dispersion curve that is fitted afterwards by the theory to calculate the material parameters. The principles of the test equipment are described in detail elsewhere [4].

Testing Top-coats for Computer Hard-disks

The hard-disk and the write-read head of computer mass-storage devices are protected by ultra-thin hard-coatings a few nanometers thick to avoid data loss in case the head hits the surface of the discs. The progress in increasing the storage density requires reducing the distance between head and disk. Therefore, thinner top-coats have to be developed with improved wear protecting properties. Tetrahedral amorphous diamond-like carbon (ta-C) that can be deposited as super-hard film is a promising material for this application. This can be made by plasma deposition technology [5]. The mechanical test of such films in the range of few nanometers thickness is a challenge for the test methods available. Figure 2 shows dispersion curves measured by the LAwave technique at ta-C films on silicon in the thickness range from 4 to 5 nm. The films have been deposited by the Pulsed High-Current Arc (HCA) technology developed in the Fraunhofer Institute for Material and Beam Technology [6]. The high ionization degree of the plasma that can be realized by this technology enables films with a high amount of tetrahedral sp^3-diamond bonds to be deposited. For the films presented in Figure 2, the substrate temperature T_S has been varied, resulting in dispersion curves of different slope. The highest elastic modulus, also termed Young's modulus E, is calculated for the sample with the highest slope of the dispersion curve. The results reveal that deposition at room temperature T_S = RT produces films with the highest Young's modulus. Increasing the substrate temperature T_S causes the elastic modulus to reduce. This behavior can be explained by the increasing mobility of the carbon atoms deposited in the film, promoting the formation of graphitic sp^2-bonds instead of sp^3. A higher Young's modulus is also a measure for higher hardness that can hardly be determined for such thin films. A relation of $H \geq E/10$ has been found for thicker ta-C-films [7].

The diagram in Figure 3 depicts the effect of the film thickness d in the range from 3 to 90 nm on the Young's modulus E. The film property is nearly constant in the range above 20 nm. However, below 20 nm film thickness the Young's modulus gradually decreases from 650 to 400 GPa. This behavior can be explained by a soft graphitic layer at the very top of the film. Such ta-C-films grow by carbon atoms shot with high energy beneath the surface. The internal stress there causes them to arrange in the structure of tetrahedral sp^3-bonds. However, ions with lower energy or low impact angle penetrate not so deep and form the uppermost atom layers, where the stress vanishes and the atoms arrange in graphitic bonds. With reducing total film thickness, the effect of the graphitic layer increases compared to that of the hard-coating and the Young's modulus calculated for the total film reduces noticeably. With a double layer model, the graphitic layer thickness has been estimated in a range of between 1.3 to 2 nm depending on the total film thickness.

The wear resistance of the top-coats can be characterized by the scratch resistance. Figure 4 proves a clear correlation between the Young's modulus and the scratch resistance to exist for the nanometer ta-C-films. The scratch resistance has been measured by atomic force microscope equipped with a diamond cantilever [8]. The tests have been done for films with $d = 5$ nm thickness. To vary the film properties, nitrogen has been incorporated into the films. Both Young's modulus and scratch resistance reduce with the nitrogen content, providing the evidence that Young's modulus and hardness correlate. This approves that the laser-acoustic test can be used to evaluate non-destructively the wear protection quality of nanometer ta-C-films.

That there is really a correlation between Young's modulus and sp^3-bond content of ta-C-films is illustrated in Figure 5 [9]. The fraction of sp^3-bonds has been measured by X-ray photo-electron spectroscopy (XPS). The bonding condition has been varied by depositing the films at different substrate temperatures T_S. With increasing temperature the film modulus E decays from 500 GPa down to 60 GPa. Likewise, the fraction of sp^3-bonds reduces from 70% down to 0%. The diagram in Figure 5 enables the content of sp^3-bonds of ta-C-films to be deduced from the quick and easy measurement of the Young's modulus by laser-acoustics.

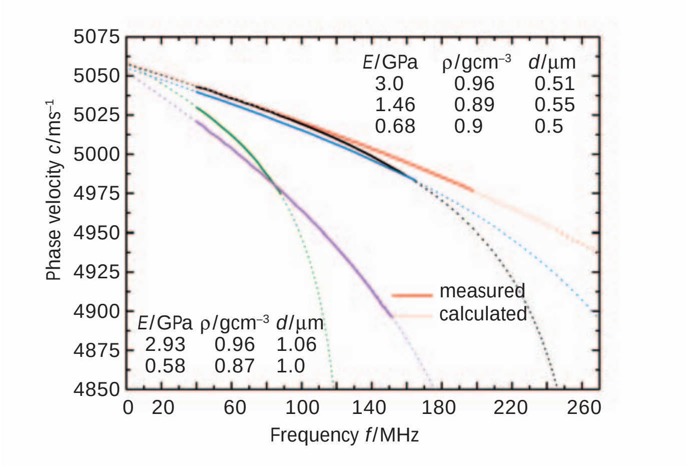

Figure 7: Laser-acoustic measuring results for two test series of porous low-k films. Contrary to the ta-C hard-coatings (Fig. 2), the dispersion curves of the low-k films decay with frequency, asserting the elastic modulus of the film to be distinctly lower than that one of the substrate.

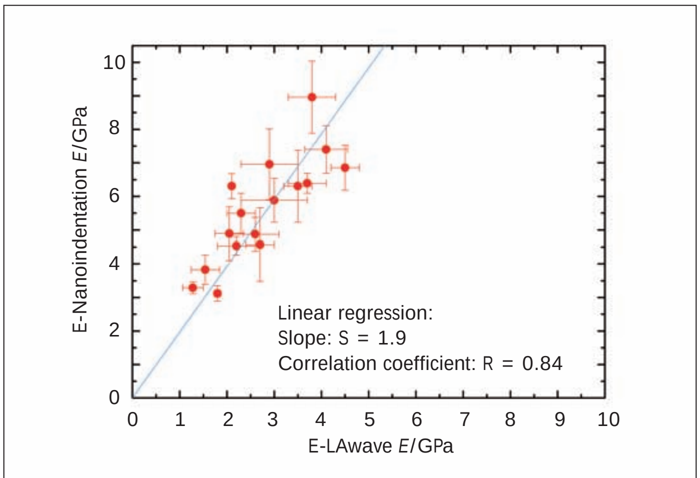

Figure 8: Comparison of the values measured by nano-indentation and laser-acoustics for porous low-k films. The linear regression yields a good correlation (R = 0.84) for the results of both techniques. However, the indentation has measured values double as high as laser-acoustics. This could be ascribed the densification of the porous structure the indenter makes beneath its tip.

Nano-porous Low-k Films

Progress of integration in the integrated circuit industry is nowadays confronted with increasing capacity between the interconnecting lines. This phenomenon increases the signal delay, cross-talk noise and energy dissipation. To overcome this problem, many efforts are undertaken to develop insulator materials with a lower dielectric constant (permittivity). Nano-porous films with a porosity higher than 40% (Fig. 6) have promising dielectric properties with a permittivity of $k < 2.3$ [10]. One of the critical points for their current application is the still low mechanical stability of the insulator films in copper damascene structures. Chemical-mechanical polishing of metal lines places high stress on the insulating film stacks that the nano-porous material has to withstand. Therefore, insulation films have to be developed with both a high porosity and the mechanical strength as high as possible. It is obvious that mechanical test methods are needed to accompany the development and to control the technology. Due to the weakness and heterogeneity of the film material, the results of techniques based on plastic imprints are influenced by the substrate with reducing film thickness, have to consider the effect of creeping of the polymeric structured material and the change of the porous structure in the plastically deformed region beneath the indentation tip. The vibrations of the surface acoustic wave provoke elastic displacements of less than a nanometer so that they do not influence the material in any way. The very fast cyclical loading the wave creates in the material is far beyond the relaxation time of the creeping process.

Figure 7 shows laser-acoustic results measured for two test series of SiCOH low-k films with different film thickness, about 0.5 and 1.0 µm. Contrary to the ta-C hard-coatings (Fig. 2), the dispersion curves of the low-k films decay with frequency, asserting the elastic modulus of the film to be distinctly lower than that one of the substrate. The curves show clear curvatures. In such a case, two parameters of the film can be calculated, Young's modulus E

and density ρ. For low-k films, *E* and ρ are interesting parameters. Young's modulus E quantifies the stiffness of the film and serves to characterize the mechanical strength. The density ρ is a measure for the porosity, an important micro-structural parameters for the high porous low-k material. The values for modulus *E* and density ρ in Figure 7 suggest that the Young's modulus of the high porous films investigated could be increased by half a magnitude with the density remaining nearly unchanged. This proves a successful step to have been completed in these test series to reinforce the porous structure of the films without loosing the amount of porosity.

From a technical viewpoint, characterizing thinner films than shown in Figure 7 is of essential interest. Therefore, the effect of film thickness on the results has been studied [11]. It has been found that with the LAwave system both parameters, *E* and ρ, can be measured up to film thicknesses down to about 150 nm with acceptable uncertainty. Below this limit, only the film density can be determined.

The laser-acoustic test results for the Young's modulus have also been compared with those of indentation test (Fig. 8) [12]. The linear regression yields a good correlation (R = 0.84) for the results of both techniques. However, the indentation has measured values double as high as laser-acoustics. This could be ascribed to the densification of the porous structure the indenter makes beneath its tip. For dense film materials, indenter and LAwave yield values of very good agreement as has been demonstrated for hard-coatings [13].

Subsurface Damage in Semiconductor Wafers

Cutting, grinding and polishing surfaces of semiconductor wafers gives rise to the creation of defects in the region beneath the surface, termed subsurface damage. Optimizing the processes of sawing the waver from ingot and removing the material of the defective surface zone is an essential factor for low costs, high quality and high reliability in wafer manufacturing. Therefore, it is very useful to have reliable methods for characterizing the subsurface damage.

Figure 9 shows LAwave dispersion curves measured at silicon wafers with three different states: sawn from the ingot, after having removed a part of the subsurface damage by etching and grinding and the polished final state. For the as-sawn state, the curve drastically decays with frequency. This can be explained by the subsurface damage forming a layer with an elastic modulus distinctly lower than that of the non-damaged substrate. After having partly removed the damage, the dispersion curve has a lower slope. For the polished final surface state, the dispersion curve is simply a straight line parallel to the frequency axis which is the typical LAwave result for completely homogenous test samples. At the frequency *f* = 0 MHz, all curves meet in the same point, the velocity of the non-damaged substrate.

This behavior of the dispersion curve has suggested using the LAwave technique for determining the depth of the subsurface damage [14]. The test consists of three steps: the dispersion curve is measured, the slope of the curve is calculated by linear regression and the slope is transferred to a calibration table to find the related damage depth by interpolation. The calibration table has been established from measurements at reference wafers. The damage has been definitely removed step by step by dry etching to the depth where the dispersion is in the range of the measuring uncertainty. From the weight lost of the wafer, the damage depth can be determined for each removal step afterwards. A special version of the LAwave system has been developed and transferred to the industry that can test wafers until 300 mm diameter (Fig. 10).

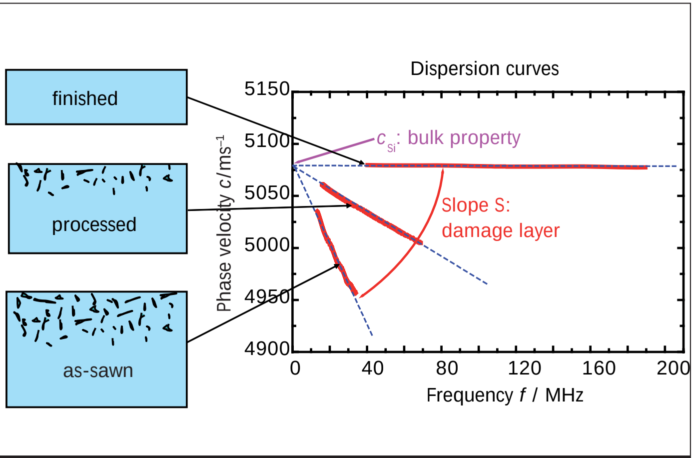

Figure 9: Dispersion curves measured at silicon wafers as-sawn from ingot, non-completely processed, finished. At the frequency *f* = 0 MHz, all curves meet in the same point, the velocity of the non-damaged substrate.

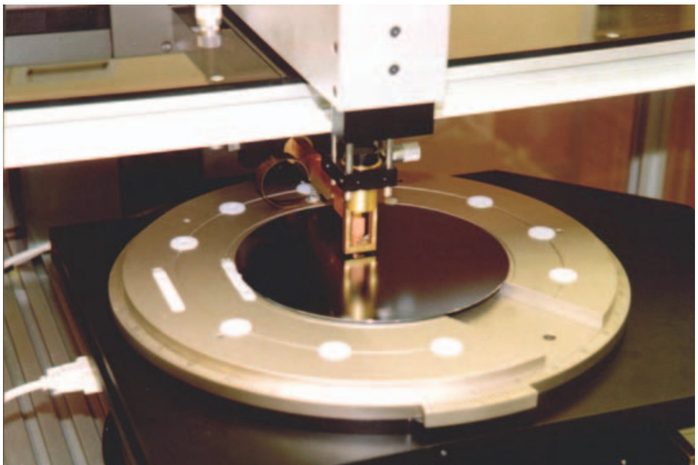

Figure 10: LAwave tester for 300 mm wafer. A special version of the LAwave system has been developed and transferred to the industry that can test wafers until 300 mm diameter.

The diagram in Figure 11 illustrates an example that more sophisticated conclusions can also be drawn from LAwave tests. It shows profiles of the Young's modulus for wafers cup-grinded with different technological parameters, as grit size of the grinding particles d_g, cutting speed v_c and feed rate v_f. The profiles have been obtained from wafers whose subsurface damage has been stepwise removed by reactive ion etching. The dispersion curve of the surface acoustic wave has been measured before and after each etching step. A difference curve has been calculated from both measurements to isolate the dispersion the removed layer L_i causes. From the etching depth, the layers thickness d_i can be deduced. Using the theory of surface acoustic dispersion in layered materials enables one to calculate the Young's modulus of the layer etched away. The depth profile of the Young's modulus provides interesting insight into the depth distribution

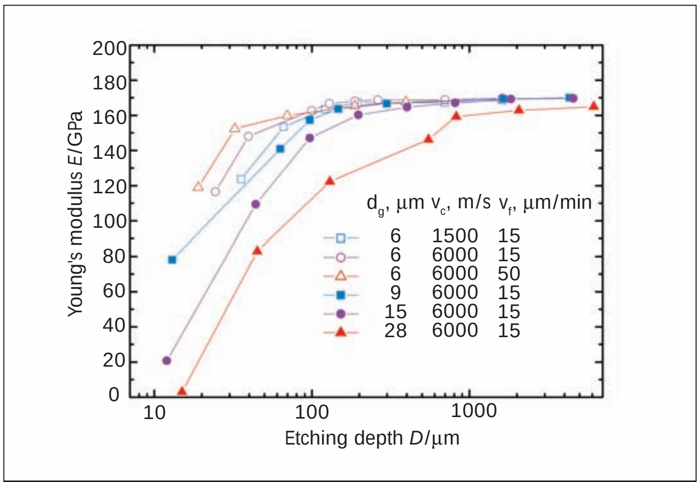

Figure 11: Profiles of Young's modulus E versus etching depth *D* for wafers cup-grinded with different grinding parameters, d_S = grit size, v_c = cutting speed, v_f = feed rate. Using the theory of surface acoustic dispersion in layered materials enables one to calculate the Young's modulus of the layer etched away.

of the defects, taking into account that defects reduce the elastic modulus by making the material more compliant.

The profiles in Figure 11 reveal that the highest defect density exists within in the surface region of 20 nm deep. For grinding with course grain (diameter: 28 µm), the Young's modulus reduces down to the extremely low value of less than 10 GPa compared to that of perfect silicon, 169 GPa. This suggested that completely damaged and only loosely connected material predominates within this depth. The modulus does not depend on the measuring direction, indicating the crystallographic orientation of the single crystal has been lost. Grinding with smaller grains and more moderate parameters results in higher values for Young's modulus within the upper layer. The degradation is distinctly lower and many material regions still stick together. With increasing etching depth the elastic modulus increases and approaches gradually the value of the non-damaged silicon, 169 GPa. The detectable damage has been removed when the modulus value of the perfect silicon substrate is reached. This point in the profile depends considerably on the machining parameters.

The shape of the profiles enables a three-zone model to be established for the gradient of the damage structure [15]. Zone 1 is only some ten nanometers thick and consists of very defective material characterized by a low elastic modulus. Grinding with large grit size (28 µm) triggers a brittle damage mode which is very effective for rapid material removal. The material particles only loosely cohere at the surface. Reducing the grit size increases the Young's modulus in zone 1 by magnitude. The material removing process changes to the ductile mode, characterized by still substantial coherence between the damaged particles at the surface.

Zone 2 consists of material with medium defect density. It has been defined to range to the point where the modulus of the non-damaged material is reached. Laser-acoustic measurements done in different crystallographic directions revealed a preferential orientation of the defects parallel to the crystallographic orientation [110] known to be the main cleavage plane of silicon. The depth of zone 2 sensitively depends on the grinding process. Grinding in the brittle mode (grit size: 28 µm) extends zone 2 to more than 6000 nm, whereas for the ductile mode (grit size: 6 µm), zone 2 has only a depth of approximately 160 nm.

Zone 3 consists of low defective material that has the same preferential orientation as zone 2. For this zone, the dispersion curve has still a detectable slope differing from the constant velocity obtained for the final polish state (Fig. 9). However, the Young's modulus does not significantly differ from the value of the perfect silicon crystal any more. Zone 3 is completely removed, if the velocity of the surface acoustic wave is independent on the frequency within the error range.

Summary

The laser-acoustic technique LAwave can be used for solving a variety of problems of surface characterization related to nanotechnology. For the example of diamond-like carbon top-coats for computer hard-disks, it has been demonstrated that the mechanical behavior of ultra-thin films can be characterized. The elastic modulus yielded by the tester is sensitive to the deposition condition and enabled to conclude to a double-layer structure of the nano-films, consisting apart from the hard-coating on very thin soft graphitic layer.

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Dr. Andreas Leson studied physics at the Institute of Applied Physics at the University of Münster where he recieved his PhD in 1986 in experimental physics with the subject magnetism. From 1987 to 1989 he was a scientific staff member at the Krupp Research Institute in Essen. And from 1989 to 1997 Leson worked as a technological consultant at the Verein Deutscher Ingenieure (VDI) in Düsseldorf. Since 1997 he is Vice Director of the Fraunhofer Institute Material and Beam Technology. As in many other committees Andreas Leson is member of the NanoS Advisory Board.

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