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MEASUREMENT OF MOLECULAR SUBMONOLAYERS

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Abstract: This paper describes a measurement technique (submonolayer ellipsometry) that can be used for the measurement of very thin layers and submonolayers (monolayers that do not cover the whole surface of a substrate). Ellipsometry is a very old common known technique in form of Nullellipsometry, Rotating Polariser, Rotating Compensator and Rotating Analyser Ellipsometry for the measurement of thin films. But for the measurement of very thin films these techniques are not useful, because Rotating Analyser, Rotating Compensator, Rotating Polariser Ellipsometers are from theory and praxis not able to measure very thin films correctly and Nullellipsometers have drift problems of the compensator anisotropy and have a too long measurement time. In this paper we describe an ellipsometer that has not this disadvantages and can measure the thickness of a submonolayer with a precision of about 0.002 nm in 4 seconds. The potential of the instrument is shown by some measurement examples where the locking of organic nano-sized molecules to a surface or to other molecules is measured.

Keywords: Ellipsometer, Monolayer, Molecule

1 INTRODUCTION

Ellipsometry is a very old technique, that is more than 100 years old. The first time it was mentioned in the Göttinger Nachrichten on 14. July 1888 [1]. From this time several developments are made in the field of ellipsometry. A commonly known ellipsometer type is the Nullellipsometer which has three movable optical components, a polariser, a compensator and an analyser. All these components are moved by iterative minimum search until the detector of the instrument sees an absolute intensity minimum. This is a very time consuming process which can take 5 minutes or more. To avoid this problem so called Rotating Analyser, Rotating Compensator and Rotating Analyser Ellipsometers are developed. These instruments have only one moving component and so they can measure very fast. The measurement time can go down to 1 millisecond or less. But these instruments have the big disadvantage that they can not be used for the measurement of thin layers below 10 Nanometers. From theory real rotating analyser ellipsometers must show systematic errors in the order of 10 Nanometers. This theoretical value is confirmed by practical tests with reference wafers (10 nm SiO_2-layer on silicon substrate). To avoid this problem we developed a Submonolayer Ellipsometer that has a better precision as an Nullellipsometer because it uses no compensator and that measures very fast.

2 THE SUBMONOLAYER ELLIPSOMETER

Heart of the Submonolayer Ellipsometer (figure 1) is an error corrected stepper motor with a physical step width of 0.001° and a virtual resolution of 0.0001°. The virtual resolution is the mathematical calculated reproducibility of the instrument. By use of an interpolation this is the effective angle resolution of the instrument. The absolute precision of the stepper motor is 0.002°. To get this high precision the errors of each motor are measured contactless and are stored in an error correction table. The maximum step rate of the stepper motor is 720 000 steps/second.

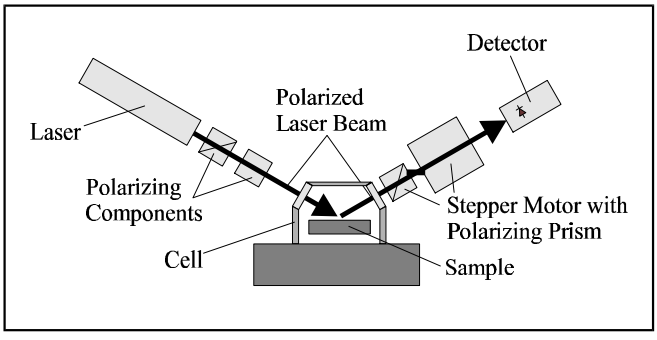

Figure 1. Build-up of the Submonolayer Ellipsometer

The build-up of a Submonolayer Ellipsometer (figure 1) is similar to the build-up of a rotating analyser ellipsometer. A light source (in this case a laser) produces polarised light. The state of polarisation is manipulated by some optical polarising components before the laser beam hits the sample. The reflected light passes the hollow shaft of the stepper motor and hits a detector. On the stepper motor is a polarising prism mounted that polarises the reflected light linearly before it hits the detector. Now if the motor would rotate permanently the instrument would have the same problems as Rotating Analyser Ellipsometers when measuring very thin films. To avoid this problem a new measurement algorithm is developed.

Figure 2 shows the state of polarisation of the electromagnetic wave that will pass the stepper motor with polarising prism. At first the ellipsometer searches the angle where the electromagnetic field strength has a minimum (marked as point A in figure 2). Is this angle found with a reproducibility of 0.001° or better the ellipsometer measures the field strength and also the field strength at an orthogonal angle (marked as point B in figure 2). The state of polarisation is calculated directly with these data.

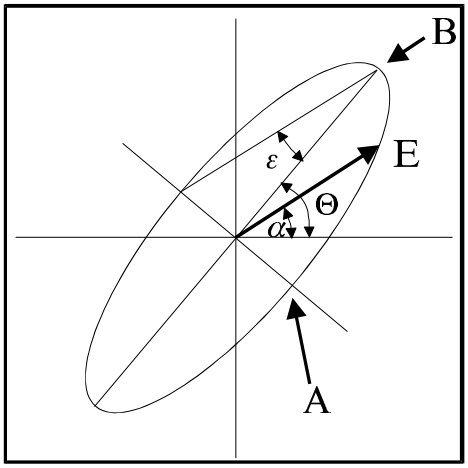

Figure 2. This diagram shows the state of polarisation after the sample. The elliptical polarised light wave is described by two quantities, the ellipticity ε and the orientation Θ. E represents the electromagnetic field strength vector.

3 MEASUREMENT OF VERY THIN FILMS

A Submonolayer Ellipsometer can be used for several applications. One typical application is the production control of very thin layers of laser diodes with a thickness of 5 or 10 nm. Commonly known Rotating Analyser Ellipsometers or Rotating Compensator Ellipsometers have a permanently rotating optical component which produces an sinusoidal intensity signal at the detector site. Making FFT-analysis or a harmonic analysis three quantities (amplitude, signal offset and phase shift) are calculated in direct or indirect form.

A measurement made with a conventional Rotating Analyser or Rotating Compensator Ellipsometer does not give correct measurement results if the received light is linear polarised. For linear polarised light no ellipticity ε (see figure 2) is existing the ellipse is now a straight line. For a definite angle a, the minimum angle, is no field strength E and no intensity existing. When making a FFT-analysis or a harmonic analysis the calculation will always give a small ellipticity caused by optical component errors or quantisation errors of the D/A converter. This ellipticity error is commonly known as the D=0° and the D=180° problem. D is one of the result quantities given by an ellipsometer [2]. It characterises the relative phase shift between the input and the output field strength vectors and is a quantity that characterises the sample. An ellipsometer normally also gives a second quantity the so-called y-value. Both values can be used for calculation of film thickness.

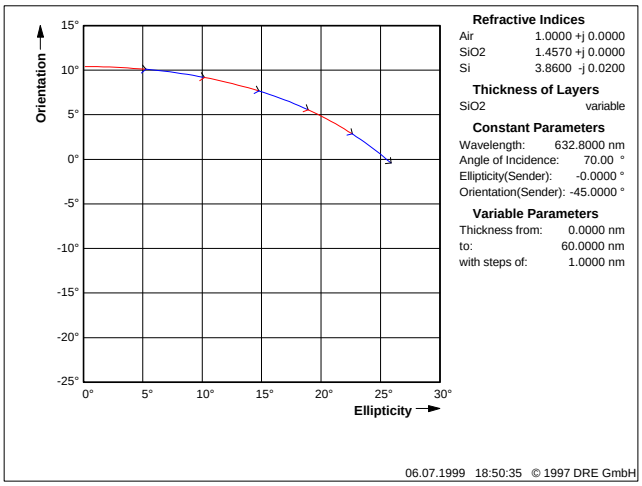

Figure 3. Simulation of a thin SiO_2 layer on silicon bulk material. The incident light is linear polarised.
The simulation curve is interrupted every 10 nm by an arrow.

Samples with very thin films will give D-values in the neighbourhood of 180° if the imaginary part of the refractive index of the coated bulk material is very small. Such samples are for example coated glass and silicon samples. Figure 3 shows the theoretical behaviour of the polarisation defining quantities ellipticity ε and orientation Θ (definition in figure 2) for silicon bulk material.

Is the incident light linear polarised then the reflected light is also nearly linear polarised (ellipticity»=0°), so the D=180° problem appears. With realistic Rotating Analyser Ellipsometer build-ups the errors are in the magnitude of 10 nm for a 10 nm layer.

To solve this problem sometimes the incident polarisation is changed to circular state of polarisation by use of a quarter wave plate. With such a quarter wave plate the simulation diagram changes to the diagram shown in figure 4. Now the D=180° problem appears for a layer thickness of 60 nm. For very thin layers is the ellipticity in the magnitude of 10° what is acceptable for a Rotating Analyser Ellipsometer. But a quarter wave plate is used and high end quarter wave plates have retardation errors in the magnitude of 0.5% what is corresponding to a D-error of approximately 0.45° or an ellipticity error of 0.223°. Such an ellipticity error would produce a systematic layer thickness error of about 10 nm what can be taken from figure 4.

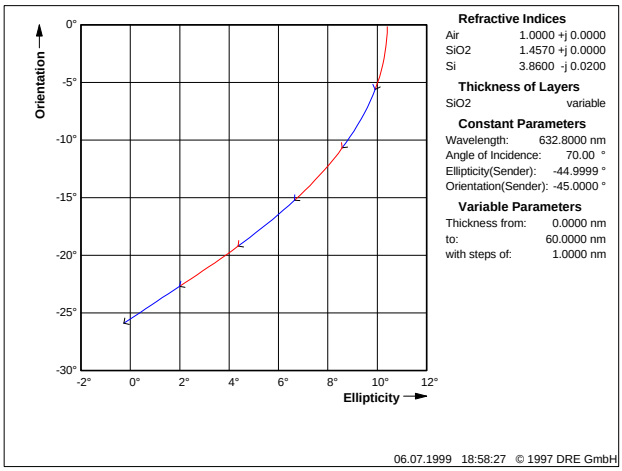

Figure 4. Simulation of a thin SiO_2 layer on silicon bulk material. The incident light is circular polarised.
The simulation curve is interrupted every 10 nm by an arrow.

So it can be seen easily that the physical principle of a Rotating Analyser Ellipsometer is not useful for very thin layers. Practical tests on very thin layers in semiconductor industry have validated this theoretical estimation.

The Submonolayer Ellipsometer described in this paper has a similar build-up as an conventional Rotating Analyser Ellipsometer, but instead of a permanently rotating analyser it uses the stepper motor that can make a positioning with very high precision. At first the instrument searches the relative intensity or field strength minimum that is at point A in figure 2. This gives the orientation Q. In the next step the intensities are measured in point A and B. This gives the ellipticity e. Now the ellipsometric quantities are calculated without use of FFT-analysis or harmonic analysis.

The advantage of the measurement algorithm is that it shows best precision for linear polarised light and very thin layers. The film layer thickness errors are reduced from 10 nm to 0.002 nm for a SiO_2-layer on silicon bulk material with the new measurement algorithm. The reproducibility of the instrument is now in the magnitude that it can be used for example for characterisation of the cleaning processes of very pure silicon wafers. Tests that we made in co-operation with semiconductor industry showed clearly that the Submonolayer Ellipsometer can be used for optimisation of cleaning processes and it can also be used for the optimisation of clean room wipers.

4 MEASUREMENT OF MONO-LAYERS

The high reproducibility of the Submonolayer Ellipsometer opens new applications for an ellipsometer. One application that was dominated before by Nullellipsometers can now be opened for this new type of ellipsometer. Nullellipsometer have a very high reproducibility but they have the compensator precision problem and they are very slow. So it makes not sense to use such a system for in-situ measurements of the build-up of monolayers.

Some working groups have tried to solve the speed problem of a Nullellipsometer simply by defining a relative minimum to be an absolute minimum [3]. But when doing this the locking kinetics is low passed and one gets not correct information on the locking process.

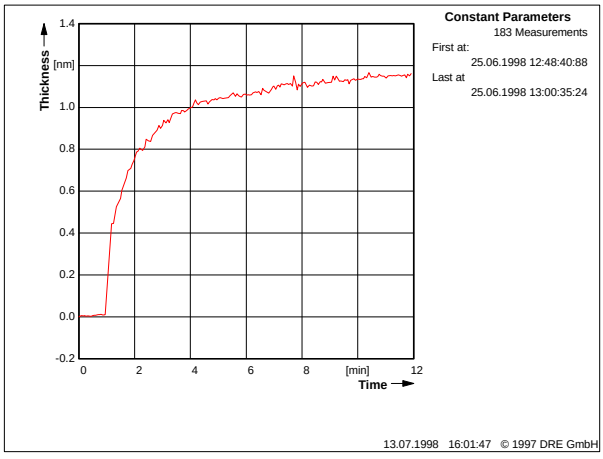

Figure 5. Locking of tensid molecules to gold bulk material. After 12 minutes the monolayer is build up

The Submonolayer Ellipsometer is in contrast to a Nullellipsometer fast enough to measure kinetics of a locking process in a liquid. Figure 5 shows as an example the locking of tensid molecules to a gold surface.

The measurement was made in a cell as shown in figure 6. The laser beam enters the cell through a glass window and it leaves the cell through a second glass window.

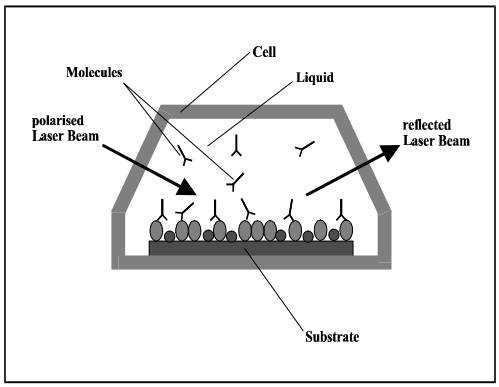

Figure 6. Cell for in-situ measurement of the locking process of molecules

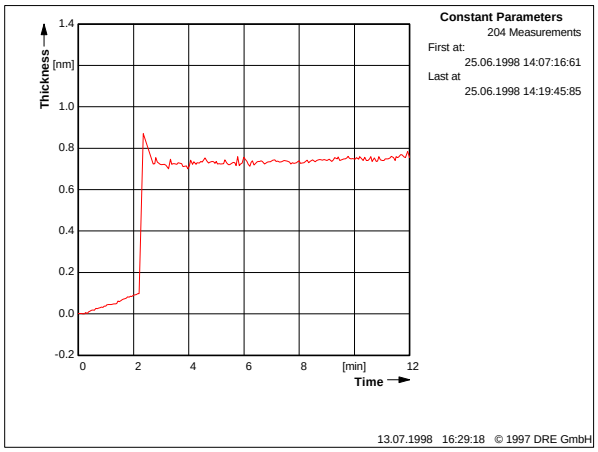

Figure 7. Locking of tensid molecules with high affinity to gold bulk material. After some seconds the monolayer is build up

The advantage of the new submonolayer ellipsometer type can be demonstrated for a very fast locking process. Figure 7 shows such a fast locking process. In this case is the liquid contaminated. So for the first 2 minutes dirt is locking to the gold bulk material. Then after adding the tensid molecules a monolayer is build up within some seconds. Then in the next step the dirt is removed from the surface by the small tensid molecules. A stable monolayer exists. These two examples demonstrate the performance of the Submonolayer Ellipsometer for the measurement of monolayers.

5 MEASUREMENT OF ANTIGEN-ANTIBODY REACTIONS

A field for this type of ellipsometer is the measurement of molecular locking effects of biological nano-sized molecules. Figure 8 shows the principle of such an application. On the substrate are antigens bound. These antigens form a submonolayer on top of the substrate. If molecules (in this case antibodies) are locking to the antigens, the submonolayer is modified to a changed submonolayer. The change of the submonolayer is a measure for the number of molecules that are locked to the antigens. From this point of view the submonolayer ellipsometer can be used for medical diagnosis of diseases.

Figure 9 shows a measurement diagram for this type of application. Antigens for Anti-Myloperoxidase Auto-Antibodies (Anti-MPO) are locked to a solid phase (substrate in figure 8). Then in the next step 15 ml buffer solution is filled in the cell and the basis line is taken. Small unspecific locking appears. Then the antibodies are filled in so that the solution has a concentration of 20 U/ml. This concentration is comparable to the sensitivity border of conventional diagnostic ELISA-tests. This example shows that a Submonolayer Ellipsometer can be also used for medical research or medical diagnostics. In this case the antibodies have a size of about 160000

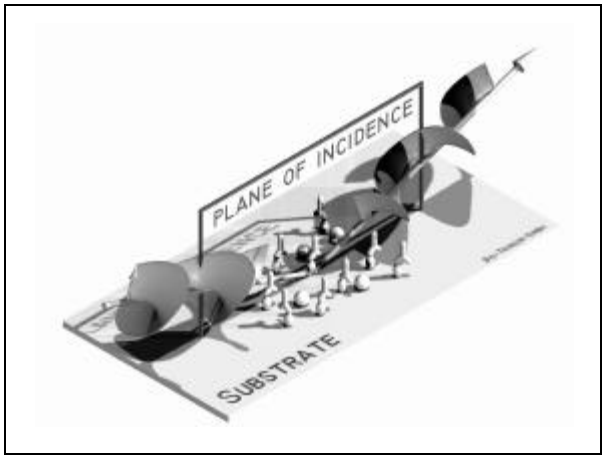

Figure 8. Receptor molecules are bound to a substrate and are forming a submonolayer. If other molecules lock to these molecules the submonolayer is changed. This figure also shows the laser beam, its field strength vector and the shadow of the field strength vector.

Dalton (hydrogen equivalents). The antibodies are big biological macromolecules. Macromolecules have a different type of locking kinetics compared to small molecules like tensid molecules as shown in figure 5 and 7. Macromolecules show a more rough kinetics (see figure 9). The reason for this is statistics. When measuring the build-up of a tensid monolayer a big number of molecules is locking to the surface. So the locking rate can be described by the affinity to the surface. Macromolecules are clumping and only a small number of molecules are locking to the surface. So the locking process is described by statistical locking events and the curve can not be so smooth as expected from the affinity function.

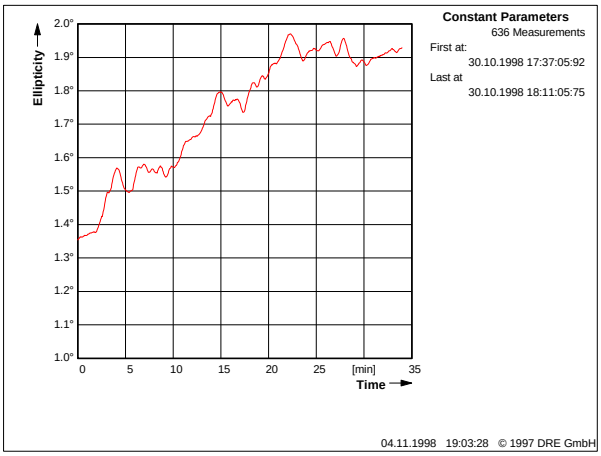

Figure 9. Measurement of Locking of Anti-Myloperoxidase Auto-Antibodies (Anti-MPO) to a solid phase with immobilized antigens.

6 DIRECT VIRUS DETECTION

Viruses are big macromolecules. It was expected that the locking process is similar to that of antibodies. But when measuring kinetics we found a strange unexpected behaviour. Figure 10 shows locking kinetics of viruses to it's antigens. The volume of the cell was 20 ml and a virus had to pass 2 mm buffer solution until it can lock to it's antigen. We have expected a locking time of about 20 minutes or more and found a locking of all viruses within 30 seconds. It seems as if there is a unknown long distance force that brings all viruses to the target. We think the reason for this fast locking process is the wave structure of viruses. May be viruses use an unknown mechanism based on wave theory to find there targets. The Submonolayer Ellipsometer can be an instruments to check our hypothesis.

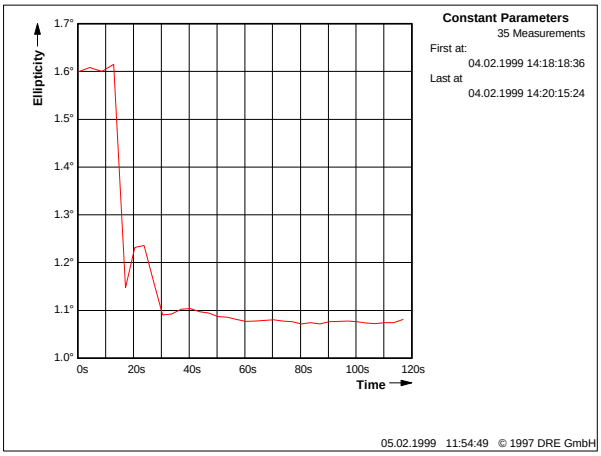

Figure 10. Locking kinetics of a virus to a solid phase equipped with antigens.

7 DNA DETECTION

Hybridisation of DNA is also a submonolayer locking process. Figure 11 shows the principle of DNA-detection. DNA-probes are covalent locked to the solid phase. Then the sample is incubated with denaturalised DNA fragments under special conditions. Now they are locking to the probes (hybridise) and the state of polarisation of the reflected beam is changed. Figure 12 shows the measurement result for a DNA-chip prototype. For this measurement the Submonolayer Ellipsometer was equipped with a xy-translations table.

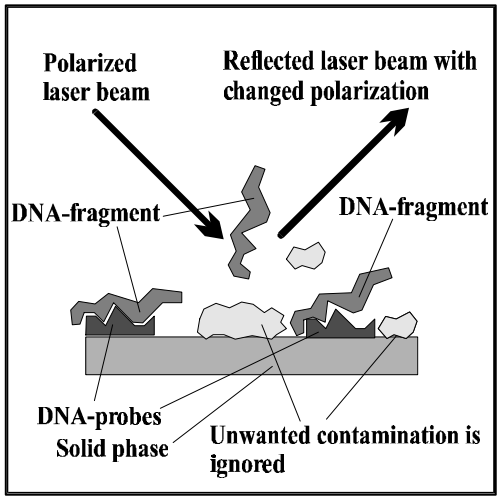

Figure 11. Principle of DNA-analysis

8 SUMMARY

A new type of ellipsometer enables the measurement of very thin films and so-called submonolayers with high reproducibility and absolute precision. The heard of this type of ellipsometer is an error corrected stepper motor that rotates very fast and precise. All measurement quantities are related to absolute physical quantities and so this type of ellipsometer does not uses reference wafers as calibration standard.

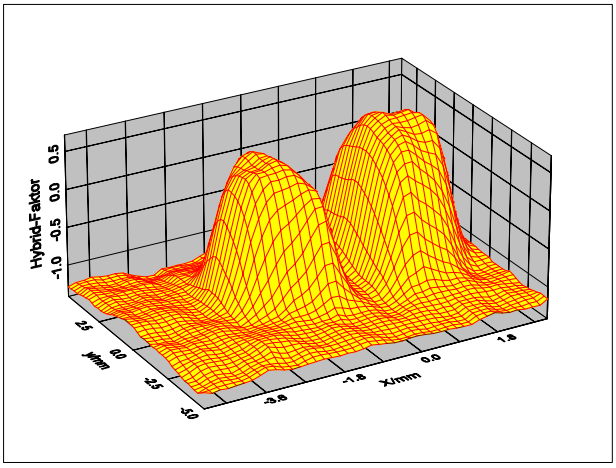

Figure 12. Measurement protocol of a DNA-biochip prototype. Two positive hybridisation events are recognised.

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