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Study on Temperature and Etching Effects on Silicon Oxide Formation Using Laser Ellipsometric Method

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Abstract

In this paper, a laser ellipsometric method is implemented to study the formation of oxide films on silicon substrate at room temperature in air. Two lasers, He-Ne and semiconductor diode, as well as a tungsten halogen lamp, were used as a light source in this method to show the importance of coherency for accurate results. The thickness of oxide layer was measured and the results is compared with that calculated for a monolayer of oxide. Behavior of thermally formed oxides was studied using ellipsometry to determine polarizer angle as a function of etching time.

Keywords: Native Oxides, Ellipsometry, Silicon Devices, Laser Polarization

دراسة تأثير درجة الحرارة والتنميش في تكوين أوكسيد السيليكون بأستخدام طريقة تدوير مستوى استقطاب الليزر

الخلاصة

في هذا البحث استخدمت طريقة تدوير مستوى استقطاب شعاع الليزر لدراسة تكوين أغشية الاوكسيد على قاعدة سيليكونية في الهواء عند درجة حرارة الغرفة استخدم نوعان من الليزرات الأول ليزر الهليوم–نيون والثاني ليزر أشباه الموصلات كما استخدم مصباح التنكستن كمصادر ضوئية في هذه الطريقة لبيان أهمية التشاكه على دقة النتائج.

جرت قياس سمك طبقة الاوكسيد ومقارنتها بالنتائج المحسوبة لطبقة أحادية من الاوكسيد . جرى دراسة سلوك الاكاسيد المتكونة حراريا باستخدام تقنية تدوير مستوى الاستقطاب لتحديد زاوية الاستقطاب كدالة لزمن التنميش.

INTRODUCTION

In all applications of electronics and optoelectronics devices, oxide layers have very important roles in featuring of such devices since they are definitely being included in the structure, hence the operational characteristics, of them. The most common oxides are SiO_x, TiO, SnO_x, CdO, etc.

Many previous works on Si-SiO_x interfaces have indicated that these interfaces are mostly of small thickness [1]. Experiments performed in order to introduce the structure of such interfaces have presented increasing understanding about the formation of oxide layers and how to make use of them to enhance the interface characteristics [2-3]. Recently, a renewed interest in thin-layer oxide formation on silicon has increased as well as in formation mechanisms especially chemical vapor deposition (CVD) and operational characteristics of interface in term of functions of etching time.

Thermally-formed oxide may cause a disorder to interface structure, as the interpretation of obtained results has failed due to some unknown limitation [4]. Thermal formation of

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oxides mostly causes a shrinking in silicon-device dimension [5], but efforts to form very thin layers of oxides may eliminate or limit its effect.

Optical ellipsometry is often used to study the formation of thin films on substrates. When a thin film is formed on a metal surface, then data of ellipsometry in general will depend on the optical properties of the film and the metal, the angle of incidence, the wavelength of light, and the index of refraction of the material surrounding the sample. Ellipsometry is a sensitive optical technique for determining properties of surfaces and thin films. If linearly polarized light of a known orientation is reflected at oblique incidence from a surface then the reflected light is elliptically polarized. The shape and orientation of the ellipse depend on the angle of incidence, the direction of the polarization of the incident light, and the reflection properties of the surface. The polarization of the reflected light can be measured with a quarter-wave plate followed by an analyzer and the orientations of the quarter-wave plate and the analyzer are varied until no light passes though the analyzer [6-9].

Ellipsometer measures the changes in the polarization state of light when it is reflected from a sample. If a thin film on the surface changes its thickness, then its reflection properties will also change and measuring these changes in the reflection properties can allow us to deduce the actual change in the film's thickness [6].

Figure 1 shows a schematic diagram of a basic null-calibration ellipsometer with a quarter-wave plate positioned before reflection; *L* represents an unpolarized monochromatic light source. This light source is highly collimated with a small beam divergence such as a low power laser that serves this purpose well. *P* is the polarizing prism, *Q* is the quarter-wave plate compensator, *S* is the sample under study, *A* is the analyzer prism and *D* is the light detector. Some lasers produce linearly polarized light and when a polarized laser is used, then the light is circularly polarized just after it emerges from the laser using a quarter-wave plate.

The polarizer following the light source is a high quality prism mounted in a holder that can be rotated about an axis parallel to the direction of the light beam. The holder is calibrated and graduated so that the angle between the transmission axis of the polarizer and the plane of incidence (the plane in which the figure is drawn) can be accurately measured. This angle is measured from the plane of incidence to the polarizer transmission axis with the positive direction being counterclockwise for an observer looking into the light beam; i.e., the observer is looking in the direction opposite to the direction that the light is traveling.

A high-quality compensator following the polarizer is the important part of a good null-calibration ellipsometer. The compensator is mounted in a holder so that its plane is perpendicular to the light beam and the angle θ, measured from the plane of incidence to its axis, can be measured. A perfect quarter-wave

plate would introduce a relative phase change of 90 between two perpendicular linear components of the light and does not affect the light in any other way. Despite a perfect quarter-wave plate cannot be obtained, there are quarter-wave plates that are close enough to perfection so that any small imperfections can be ignored and it is assumed to be ideal. This is desirable to be done in part because the equations used for description of the behavior of light as it passes through the ellipsometer are much simpler with a perfect quarter-wave plate.

The environment and form of the sample under study, which is following the compensator, depend on what it is tried to be measured. If obtaining the optical constants of a clean bare surface is required then the sample should be in an environment where it stays clean and bare. If the observation of a film that forms on the sample surface is the required then the sample must be in an environment where this can occur. However, in all cases, the sample should have a small flat specular polished area that reflects the incident light. Careful sample preparation is an important factor in obtaining consistent, reproducible, and meaningful ellipsometric data.

The analyzer following the sample is a second Glan-Thompson prism and also mounted in a holder that allows measurement of the angle between the transmission axis of the analyzer and the plane of incidence. The analyzer angle, *A*, is again measured from the plane of incidence to the analyzer transmission axis by an observer looking into the beam. Finally there is a light detector.

Using a null-calibration ellipsometer, the orientations of the polarizer, compensator, and analyzer are adjusted so that the intensity of the light reaching the detector is zero. There are many settings of the polarizer and compensator that can achieve this. However, if the compensator is set at either +45° or –45° then, with a few exceptions such as reflection from a highly anisotropic sample, it will still be possible to find a null in the light intensity after it passes through the analyzer by varying only P and A. The advantages of setting θ at $\pm 45°$ are [6-7]:

(a) The amplitude of the component of the light incident on the sample that is polarized in the plane of incidence is always the same as that for light polarized perpendicular to the plane of incidence, independent of the polarizer setting, these two incident polarizations only differ in phase.

(b) The equations used to describe the polarization of light as it travels through the ellipsometer simplify considerably with $\theta=\pm 45°$. Thus in practice a fixed-compensator at $\theta=\pm 45°$ is used and the setting of the polarizer and analyzer is varied until a null is obtained.

Two numbers are got as a null measurement is made; the angular settings of the polarizer (*P*) and analyzer (*A*) at null. Therefore computation of two characteristics of the sample from these two numbers is possible. One possibility would be the index of refraction and optical absorption of a clean optically absorbing sample. Getting a transparent film on a known substrate, the index of refraction and the thickness of the film can be deduced.

Whereas a sample consisting of a thin optically absorbing film of unknown index of refraction and thickness on a known substrate is obtained, there are three unknown parameters that determine the reflection properties of the sample and the complex index of refraction and film thickness from a single measurement cannot be determined. This represents sometimes the fundamental problem of ellipsometry.

We may meet an experimental situation where there may be several distinct films layered on the surface to be studied. It is reasonable to generalize the mathematical methods used for a single film to the situation where there are multiple films. Although the calculation of multiple-film reflection coefficients is not difficult, the use of multiple films to interpret ellipsometric data is not simple. This is because for a multiple-film system we do not measure enough numbers to deduce the values for all of the parameters. Thus for multiple film systems we must construct models and see if the predictions of the models agree with the experimental data or not. This needs some imagination and a lot of recognition since the models that we construct must have a reasonable physical basis that includes a reason why we would expect a layered set of films to form on the surface [7].

Assuming a system with two films, as shown in Figure (2), there will be four different materials and three interfaces. We can assign the incident medium as (No.1), the top film medium as (No.2), the bottom film medium (No.3), and the substrate medium (No.4). A light ray incident onto the top film will be partially reflected and partially transmitted at the interface 1-2. Part of the transmitted ray will reflect back to the interface 1-2 from the interface 2-3 and part will return to the interface 1-2 from the interface 3-4. It would appear that this approach with a multiple films system would form an infinite series. If we continue to trace rays forward and backward in the two films, then the approach will be definitely confusing. although despite it is possible to analyze such approach but practically it would be so complex for only two films.

Denoting the reflection coefficients at each interface by r_{ij}, where i denotes the medium from which the light is incident and j denotes the medium into which the light is transmitted if we have a single film on a surface then the total thin film reflection coefficient (R_t) is given by [6]:

$$R_t = \frac{r_{12} + r_{23}\exp(-id_2)}{1 + r_{12}r_{23}\exp(-id_2)} \qquad (1)$$

where is the phase shift of light in the medium and it is give by:

$$d = \frac{2pn_2 D\cos f_2}{l} \qquad (2)$$

where D is the thickness of the film, n_2 its index of refraction, ϕ_2 the angle of refraction for the light in the film and λ the vacuum wavelength of the light.

For a two-film system, the term r_{23} representing the interfacial coefficient at the interface 2-3 for the single film case, can be replaced in the multiple film case by the total reflection coefficient for everything beyond medium No.2. That is, r_{23} should be

replaced by R_{23}, where R_{23} is given by:

$$R_{23} = \frac{r_{23} + r_{34}\exp(-id_3)}{1 + r_{23}r_{34}\exp(-id_3)} \quad (3)$$

Here we have used R_{23} to denote the total reflection coefficient for everything beyond medium No.2 and r_{23} to denote the actual reflection coefficient between medium No.2 and medium No.3.

If medium No.4 is not the substrate but there are more films, then r_{34} would be replaced by R_{34} in the above equation where R_{34} is given by:

$$R_{34} = \frac{r_{34} + r_{45}\exp(-id_4)}{1 + r_{34}r_{45}\exp(-id_4)} \quad (4)$$

There is no reason to prevent using these relations in a numerical calculation involving many films as required but the calculation would become boring if it is tried to be done analytically for more than two or three films. In a numerical calculation for the reflection coefficients, the calculation is performed from the bottom up, beginning with the inner film.

If a film is formed on the surface of a sample that already has a number of films on it and if an initial null-calibration measurement is done before beginning to form the film, then one should not use a multiple film calculation. Instead, the sample is treated as a bare surface whose complex index of refraction is calculated from the initial null-calibration measurement.

In many studies, it was found that the effective refractive indices of SiC/SiO_2 are smaller than those of the oxide films on Si . They increase with oxidation time , or oxide thickness , reaching the values of Si oxide . The refractive indices also depend on the oxidation methods [13].

Infrared spectroscopic ellipsometry (IR-SE) is a nother optical technique that can measure the resistivity profiles of multiple-layered samples via the free-carrier Drude effect. Standard ellipsometric analysis techniques allow the simultaneous determination of the oxide thickness and resistivity of the underlying layers after each anodization cycle since the thickness of the consumed silicon layer can be calculated from the oxide thickness [14] .

EXPERIMENTAL

In this work, wafers of (111) silicon of ~3 .cm resistivity were polished, cleaned and finished with an HF acid dip and water rinse. Then they were divided into three groups, each group was fired to a certain temperature (900, 1000, 1100)°C in hydrogen for 10 minutes and held in dry nitrogen until used.

The ellipsometer used in this work employs a replaceable light source. Two lasers, He-Ne (632.8nm, 1mW) and semiconductor (650nm, 0.1mW), as well as a tungsten halogen lamp (546nm or 633nm) with an interference filter, were used individually in order to explain the importance of coherent light source in such method. As results obtained with semiconductor diode laser source agree to an accepted degree to those obtained with He-Ne laser, but the data presented here are with the second. The angular range of this ellipsometer is ±180° with 0.05°

angular resolution. This model can measure thickness of 3Å and refractive index of 0.01. Also, angle of incidence can be varied from 30° to 90° in step of 5°.

A silicon wafer was placed on the ellipsometer holder after rinsed in water and removed from the nitrogen cover. We started thickness measurements soon in room air. The ellipsometer was set up with (632.8nm) radiation and a 1mm-diameter beam incident at (70°) to the silicon surface as the calibration of ellipsometer led to the acceptance of an index of refraction for silicon of 4.086±0.031 [5]. This value is of importance for relative thickness measurement of oxide.

The samples were not moved during the earlier stages of formation, but were removed and replaced in the beam for the longer-term measurements. Each of data obtained is an average of three consequent reading on the ellipsometer.

RESULTS AND DISCUSSION

Figures (3-5) show the increase in the ellipsometer polarizer angle measured on the three groups of samples as a function of time at different firing temperatures and different light source used in the ellipsometer. Results obtained with the He-Ne laser seemed to be more accurate compared to the other two cases regarding the published and established data of such technique.

For very thin transparent films, the increase in polarizer angle is linearly related to the film thickness. Zero point for bare silicon was calculated from the optical constants [10] to be 44.5 degrees. Other wafers have been observed to exhibit similar behavior though differing in starting thickness and in degree of hold time at the inflection points of the formation curve.

Silicon wafers, subjected to a final HF acid dip and water rinse only, were found to start with ~6Å of film. These films approximately formed at the same average rate as these shown in Figures (3-5). Step formation was not observed and no extended effort was made to determine whether stepped formation could occur on these wafers.

Features observed in the formation curves of Figures (3-5) firstly are a relatively long induction period after an initial layer formation before a burst of formation begins at about 0.3 degrees. The rate of the most rapid formation is about 2.3 degrees per decade of time, then there are two values of thickness at which a slowing formation changes to faster rate again. These changes occur at 1.63 and 2.15 degrees. Finally a third leveling occurs after several days formation at about 2.7 degrees.

The layer observed first by the ellipsometer measurement is similar in thickness to these observed previously [10-11]. It must be a nearly complete layer as it was formed in 1 hour after exposure to air and increases only fractionally in the next hour. The ellipsometer polarizer angle changes by 6.57Å/degree for a film of index 1.46 (SiO_2) and 5.43Å/degree for material of index 1.83 (SiO). In either case, the film appears to be less little than a monolayer of oxide. The rapid formation from 0.55, 0.65 and 0.7 to 1.35, 1.6 and 1.85 degrees

respectively is about twice as fact as that observed previously.

When the HF-etched and water-rinsed samples are compared to their similarly prepared samples, the same overall formation rates are observed. From 0.3 to 2.45 degrees apparently two layers are formed. On a few samples studied, a very small change in formation rate was seen at about 1.0 degree. Assuming that there are four layers of film formation in Figures (3-5) from 0.3 to 2.45 degrees or 0.58 degrees per layer, the film can be related to an oxide formation. In SiO, the molecular spacing is 3.2Å while for SiO_2 it is 3.6Å. When combined with the polarizer angle calibration, SiO becomes 0.59 degrees per layer and SiO_2 is 0.54 degrees per layer. It then seems probable that the measurement is indicating layer by layer formation of an oxide.

Some of the same oxides formed here were identified to be essentially SiO or composite SiO-SiO_x, definitely not SiO_2 [12]. It was also found that the oxides were not the same as the thermal oxides of SiO_2. Additionally the etched silicon films were identified as having an initial oxygen content corresponding to ~2Å of oxide while the greater thickness indicated by ellipsometry is largely due to contamination. In a third point of agreement films appear to stop forming at ~14Å after several weeks time. Our four layers of oxide on a partial initial layer are a little over 14 ¦ total. It appears that the drastic cleaning procedure of high temperature firing inhibits the adsorption of contaminating layer and allows a clearer examination of the formation process by ellipsometry.

At room temperature, the oxide must also form only by the ionized species and the oxide formed is a sub-oxide [12]. It is suggested that the ionized species involved in the initial stages of silicon oxidation preferentially forms suboxides. It is at later stage that diffusing oxygen may oxidize these to SiO_2 and further proceed to react with the silicon substrate.

CONCLUSIONS

It could be concluded that the oxide formed on clean silicon substrate at room temperature tends to form one layer at a time. The layer thickness measured by ellipsometry technique is compatible with calculated for a monolayer of oxide. Controlling thermal formation of oxides on silicon has led to acceptable definition of the interface (Si-SiOx) structure which could be used to enhance their characteristics.

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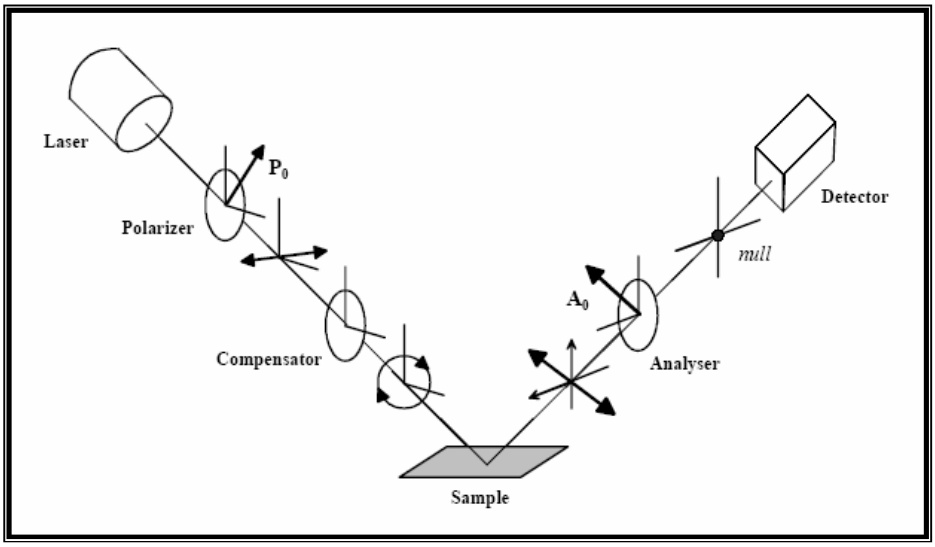

Fig. (1): A schematic diagram of a null-calibration ellipsometer

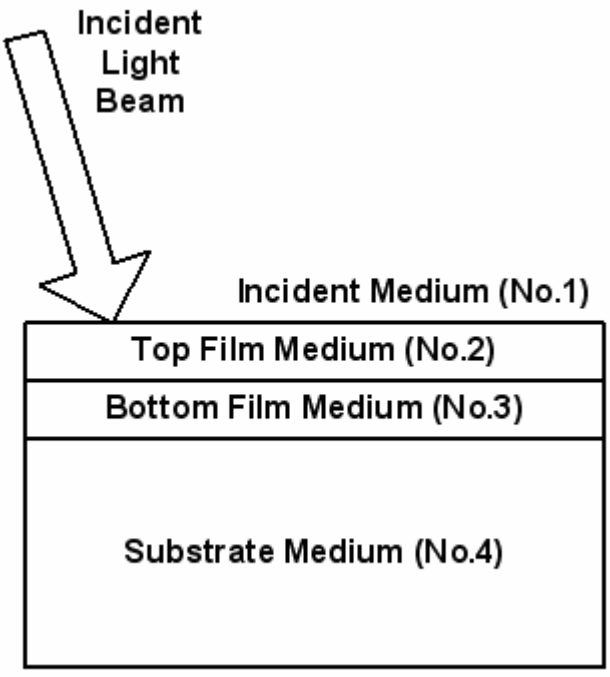

Fig. (2): The model of two-films system considered in this work

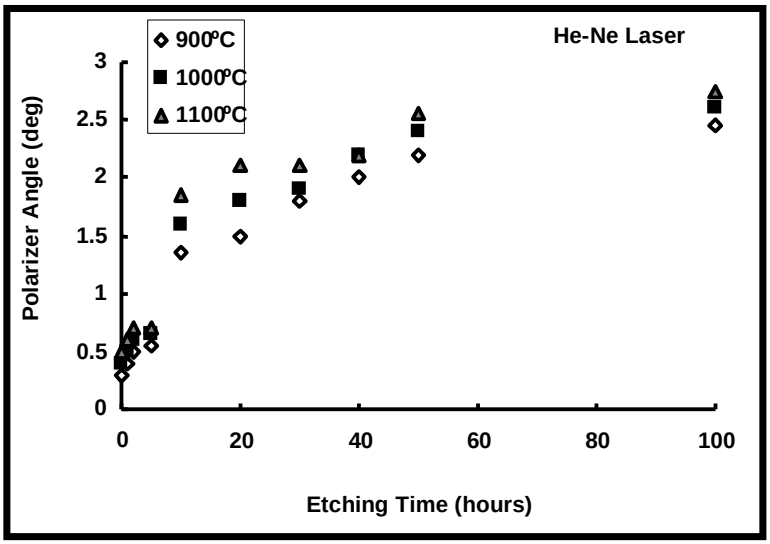

Fig. (3): Polarizer angle vs. etching time for samples fired to (900, 1000, 1100)°C using the He-Ne laser as a light source

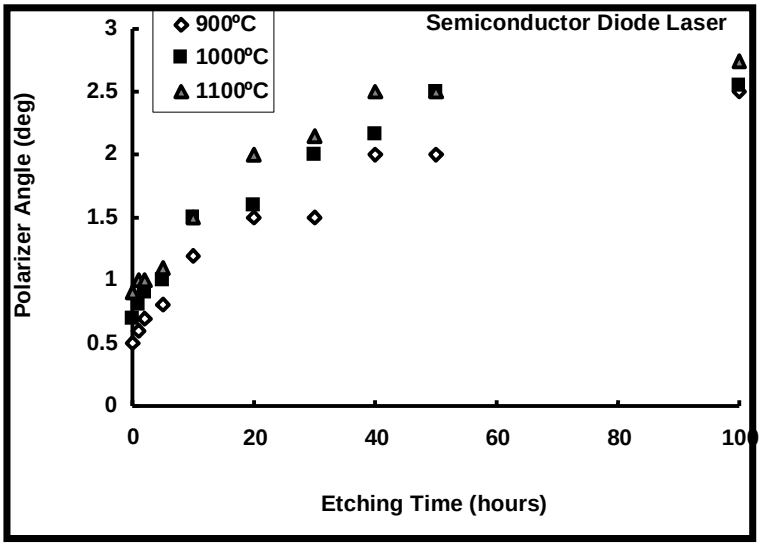

Fig. (4): Polarizer angle vs. etching time for samples fired to (900, 1000, 1100)°C using the semiconductor diode laser as a light source

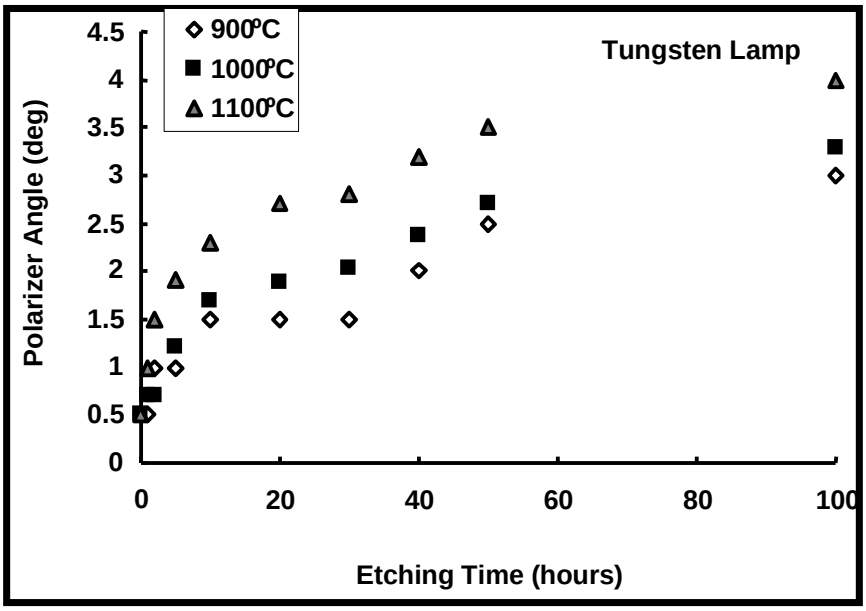

Fig. (5): Polarizer angle vs. etching time for samples fired to (900, 1000, 1100)°C using the tungsten halogen lamp as a light source