EFFECT OF PROCESS CONDITIONS ON ALUMINUM OXIDE THIN FILM USED IN pH ISFET

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Abstract

Inorganic oxide material, such as aluminum oxide, may not give linear and stable pH response as predicted from the site binding model. Investigation of the relationship between process conditions and overall film properties is described. Pyrohydrolytic aluminum oxide exhibits very distinct microscopic structures under different process conditions. The TEM results show good correlation with the leakage current and the maximum dielectric breakdown strength. These findings are useful in augmenting pH ISFET sensor design.

Introduction

With the increasing demand of miniaturized sensor for process control and monitoring in various medical and industrial applications, solid state physical and chemical sensors have gained importance from the advancement of solid state technology and physics. One type of chemical sensor is the solid state ion-sensitive field-effect transistor (ISFET) [1]. This paper focuses on the physical and electrical characterization of the chemical vapor deposited (CVD) aluminum oxide as a pH sensitive dielectric towards the development of the pH ISFET.

Various theories on the sensing mechanism of the bare gate ion-sensitive field-effect transistor (ISFET) have been developed in the past decade; such as diffusion, gel layer, ion exchange, surface state modulation, polarized interface, mobile polarizable interface and electrochemical cell. The more recent development of the site binding model such as Schenck [2], Siu [3], and Fung [4] has shed light in the modelling of electrolyte-oxide-semiconductor (EOS) and electrolyte-insulator-semiconductor field-effect transistor (EISFET) systems. Most of the theories, however, have not accounted for the relationship between the microscopic structure of the bare gate dielectric layer with its chemical response.

Based on the existing theories, the major criterion for acceptable pH sensitive gate dielectric material is that it offers a small difference between the amphoteric dissociation and association constants of the hydrolyzed surface sites. The dielectric should also have low solubility. Equally important is that the fabrication method of the pH dielectric material should be compatible with solid state technology, controllable and reproducible.

Metal oxide of the same material, such as aluminum oxide, has been reported behave differently in electrolyte environment. Abe [5] has reported that CVD aluminum oxide displayed linear pH response. Wong [6] has found diverse pH response of aluminum oxide. The diversity in the point of zero charge (PZC) of aluminium oxide in the literature is another indication that the same oxide compound may exhibits wide range of surface properties. These evidences indeed point to the importance in understanding the oxide processing conditions in order to adapt the site binding surface parameters for better interpretation

of the sensing theory of the oxide bare gate pH ISFET. These findings prompted the investigation of the relationship between process conditions and overall film properties.

This paper presents an important aspect of the oxide bare gate pH ISFET's sensing mechanism by considering the microscopic structure of the pH sensitive inorganic oxide layer with respect to its electrical and physical characteristics. The hypothesis is that these thin films, even though they are the same inorganic oxide compound, differ in microscopic structures which in turn alter the surface properties. Experimental studies presented in this paper focus on the post-annealing effect of the pH sensitive aluminum oxide layer using ellipsometry, current-to-voltage measurement technique and transmission electron microscopy.

Aluminum Oxide Deposition Procedure

Substrate Material

Silicon, moderately doped with resistivity of 5 ohm-cm, is selected as the substrate material. Two types of samples are prepared: single dielectric layer of aluminum oxide on silicon (AS) and double dielectric layers aluminum oxide-silicon dioxide on silicon (AOS). To form AOS structure, n-type (100) silicon wafers are oxidized in oxygen environment at 1050°C to form silicon dioxide layer with thicknesses between 600 to 1000 Angstroms.

Experimental Set-up

A vertical cold wall chemical vapor deposition system (Applied Materials model AMV 800) has been modified for the preparation of CVD aluminum oxide. The rotating susceptor can hold seven pieces of two inch diameter wafers in the slightly recessed areas. Susceptor temperature is monitored by a optical pyrometer above the bell jar aligned with the center of the recessed area.

Aluminum chloride, a white powder at room temperature, is sublimed above 100°C to give sufficient vapor for the CVD reaction. Its vapor pressure is approximately linear with temperature between 105°C to 125°C. The sublimator temperature is set at 115°C during CVD deposition. All gas lines are wrapped with silicon rubber heating tapes to maintain temperature higher than 130°C to minimize aluminum chloride vapor condensation [Figure 1]. Since aluminum chloride is extremely exothermic when contacts with water, small amount of moisture in the gas lines will cause the aluminum chloride to react and form undesirable aluminium oxide particulates. Precautions have been taken to minimize moisture in the gas lines.

Pyrohydrolysis of Aluminum Oxide

After thermal-grown silicon dioxide step, the wafers are immediately loaded into the CVD reaction

chamber. The wafers are then heated up slowly to avoid thermal shock. At the deposition temperature, a hydrogen annealing step is performed prior to the CVD deposition. A sufficiently high gas flow rate is needed to remove excess water vapor and by-products generated during the reaction.

Pyrohydrolysis of aluminum chloride in a hydrogen and carbon dioxide atmosphere can be written as two reactions. Firstly, hydrogen reacts with carbon dioxide to form gaseous water and carbon monoxide as by-product. Secondly, reaction of gaseous water with aluminum chloride vapor forms aluminum oxide with HCl gas as by-product. These two reactions are listed below,

and the net reaction is,

At 850°C deposition temperature, the deposition rate is approximately 160 Angstroms/min..

Figure 1. Experimental Set-up for Chemical Vapor Deposited Aluminum Oxide.

Methods of Approach

Aluminum oxide, 1000 to 2000 Angstroms thickness, was deposited onto the wafers both with and without thermally grown silicon dioxide. The samples, further annealed in different temperatures, were divided into three groups. Group one (AS) wafers, with annealing temperature equal or below 850°C, were measured with ellipsometry. Then the wafers were subjected to inert atmospheric annealing at 1000°C for less than thirty minutes and measured again with ellipsometer. The same procedure was repeated after 1175°C annealing.

Group two (AOS) wafers were metallized with aluminum dots (40 mils diameter) on top of the CVD aluminum oxide and metallization on the back of the wafer. These samples were investigated using current-to-voltage technique which was an indirect indication of the aluminum oxide film's electrical integrity in relation to processing conditions. Leakage current density and maximum dielectric breakdown strength were the measured parameters.

To correlate the microscopic structure of aluminum oxide thin films to their processing conditions, transmission electron microscopy technique was used to study grain size, film uniformity and phase. Group three (AS) wafers were cut into 3 x 3 mm² square pieces and the silicon substrates were thinned down by silicon etch. A thin aluminum oxide section was left at the center of the square piece for TEM studies.

Experimental Results and Discussions

Ellipsometer Results

Initially, aluminum oxide thickness and refractive index were measured at six different locations on wafers numbered one to six [Figure 2]. Ellipsometer results of the aluminum oxide with thickness of 1000 to 1700 Angstroms showed 1.73 refractive index. Then the wafers were subjected to annealing at 1000°C for half an hour and ellipsometry results were obtained. The wafers were further annealed at 1175°C for thirty minutes and ellipsometry results were again taken. There were no drastic change in ellipsometry results for samples annealed below 1000°C. After post annealing at 1175°C, however, the CVD aluminum oxide thickness decreased approximately 25% which indicated possible increase of film density

Figure 2. Results of Film Thickness and Refractive Index for CVD Aluminum Oxide Annealed at 850°C, 1000°C and 1175°C.

and refractive index. The variations in thickness and refractive index of such samples indicated a nonuniform shrinkage of the CVD aluminum oxide.

Electrical Characterization

Leakage current results [Figure 3], for different annealed samples, were an indication of aluminum oxide thin film's electrical integrity relating to the process conditions. Maximum dielectric strength of the CVD aluminum oxide could be an indication of the tolerance of maximum electrical field imposed on the sensor. Aluminum oxide thicknesses were measured by an ellipsometer and the results were used to calculate the applied electrical field strength across the samples. The samples, post-annealed at 850°C, 1000°C and 1175°C, under an applied voltage of 1×10^6 volt/cm indicated an increase in leakage current two order of magnitude from 5.8×10^{-9} Amp/cm² to 1.3×10^{-7} Amp/cm². At high annealing temperature, there was good correlation between the current-to-voltage results with ellipsometry results. The dielectric strength also decreased as the post-annealing time or temperature increased. Samples with a short annealing time or no post annealing showed the highest dielectric strength in the order of 4.0×10^6 V/cm.. As the post-annealing time or temperature increased, the dielectric strength was decreased to 1.4×10^6 V/cm..

Figure 3. Current Density of Post-annealed MAOS Structure as a Function of Applied Voltage.

Transmission Electron Microscopy Results

In order to further correlate the CVD aluminum oxide thin film to processing conditions, a Philips model EM 400 transmission electron microscopy was used because of its superior resolution and phase study capability compared to SEM or AUGER analytical techniques. Considered in the TEM analysis were the grain size, film uniformity, phase of the CVD film, polycrystalline or crystalline structure. At the depositing and annealing temperature of 850°C, the film appeared to be polycrystalline gamma phase with fine grain structure [Figure 4]. Diffraction pattern of the CVD aluminum oxide, deflected as a broad ring, was an indication that the sample was an amorphous solid with a small amount of polycrystalline structures.

Figure 4. TEM Results of CVD Aluminum Oxide Annealed at 850°C, (A) Grain Structure (46000x), (B) Diffraction Pattern.

The sample under annealing temperature of 1000°C had a diffraction pattern vastly different from the previous patterns. It had definite diffraction spots with a very faint ring pattern superimposed on it. The coherent scattering indicated that the structure had more of a crystalline form. In addition, from the d spacing, the phase structure of this sample was composed of gamma phase and alpha phase indicating transition from the gamma phase to the alpha phase.

For the sample annealed at 1175°C, two phases were detected, a gamma and an alpha phase. The alpha phase showed very distinct spot pattern which indicated crystalline structure [Figure 5]. At 1175°C, there was a much wider range of grain size between 0.13 to 0.54 micron. The larger grains appeared in a rectangular form with a definite grain boundary. There was a good correlation with the previous ellipsometry results; increased in film density and index of refraction with increased in temperature.

Figure 5. TEM Results of CVD Aluminum Oxide Annealed at 1175°C, (A) Grain Structure (46000x), (B) Diffraction Pattern.

Conclusion

Based on the previously suggested site binding model, pyrohydrolytic aluminum oxide has been selected as a pH sensitive dielectric with the possible improvement of the pH response over the silicon dioxide. Studies of aluminum oxide thin films, with specific annealing conditions, by ellipsometry, current-to-voltage technique and transmission electron microscopy confirm the importance of process conditions which definitely affect the relationship between the microscopic structure and the electrical properties of the oxide material. Properties of the CVD aluminum oxide, refractive index, leakage current density, electrical breakdown field strength, phase and grain size have been determined experimentally. When the CVD aluminum oxide is processed at approximately 850°C with minimal or no post annealing, the film is gamma phase with polycrystalline structure. Thus, metal oxide thin film processed differently will have diverse electrical and physical properties. It is concluded that an accurate prediction of its pH response based on the oxide surface parameters given in the literature is not possible because the processing conditions changes surface properties. These findings are useful to augment the sensor design. Furthermore, the difference on pH sensitivity and stability of aluminum oxide as a pH sensitive layer under different process conditions may be partially explained by this study.

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