Analysis Of Formation Of Silicon Nitride On Si(100) By Electrochemical Anodization Technique

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Abstract

Using electrochemical anodization technique, the silicon nitride (Si_3N_4) thin film has been deposited on the p-type Si(100) substrate at the ambient temperature. This technique is an economical and practical way to produces a very thin film like the Si_3N_4 on the p-Si substrate. Very thin nitride passivation of Si(100) stabilizes its surface or interface very well and reduces the interface states density. However, the passivated surface exhibits a substantial degradation due to the exposure to air after passivation. In this study, silicon nitride thin film have been deposited via electrochemical anodization technique on the p-Si(100) surface. Crystalline silicon has been observed by Raman spectrometry. The atomic force microscopy (AFM) have been used to carry the surface morphological properties of the deposited film. Both analysis of formation of silicon nitride (Si3N4) on the p-Si(100) and surface degradation was investigated with the high-resolution X-ray diffraction (XRD) technique.

Anahtar Kelimeler: Harran killi; Şişme potansiyeli; Metilen mavisi; Çoklu regresyon

Si(100) Üzerine Elektrokimyasal Anodizasyon Tekniği ile Silisyum Nitrür'ün Formasyonunun Analizi

Özet

Elektrokimyasal anodizasyon tekniği kullanılarak, silisyum nitrür (Si_3N_4) ince filmi oda sıcaklığında p-tipi Si (100) zemin üzerine oluşturuldu. Bu teknik p-tipi Si (100) zemin üzerine (Si_3N_4) gibi çok ince film üretmek için hem pratik hemde ekonomiktir. Si(100)'ın çok ince nitrür ile pasivasyonu, onun yüzey veya arayüzeylerini stabilize hale getirir ve arayüzey durum yoğunluğunu azaltır. Fakat, passive edilmiş yüzey daha sonra, hava pasivasyonuna maruz kalması yüzünden bozulmaya uğradığı gözlenir. Bu çalışmada, silisyum nitrür ince filmi p-Si(100) yüzey üzerine elektrokimyasal anodizasyon tekniği yoluyla oluşturuldu. Kristalize silisyum, Raman Spektrometresi ile gözlendi. Atomik güç mikroskobu (AFM), oluşturulan filmin yüzey morfoloji özelliklerini elde etmek için kullanıldı. Hem silisyum nitrür'ün p-Si(100) üzerine oluşumunun analizi hemde yüzeyin bozulması yüksek-çözünürlüklü X-ray diffraction (XRD) tekniği ile incelendi.

Key Words: Elektrokimyasal Anodizasyon, Silisyum Nitrür, XRD

1. Introduction

Dielectric thin films (SiO_2, Si_3N_4, Al_2O_3, AlN) are used for a wide range of applications in tetravalent (Si) and compound semiconductor (GaAs, InP, InGaAs) devices including ion implantation masks, passivation films, optical coatings, and wave guides for both electronic

and optoelectronic applications. Recently, low-temperature growth of dielectric films has received a lot of attention for a study of microelectronic components; mainly because low-temperature processes minimize the incongruous loss of the V group element of the III-V semiconductors [1].

Since it was first reported in 1965 by Sterling and Swann [2] that silicon nitride (Si3N4) could be used as surface passivation films in integrated circuit (IC) [2,3], silicon nitride films, in particular, have been widely used in IC processing as dual dielectric gate films, local oxidation masks and surface passivation films due to their superior electronic properties such as high dielectric constant, stability and strong resistance to diffusion.

Gate dielectric scaling requires new materials with dielectric constant (K) higher than SiO2 to provide the increased capacitance without compromising gate leakage current. One such material is Si_3N_4 that has approximately twice the dielectric constant of SiO_2 , and additionally is effective in blocking diffusion of dopant such as boron. Si_3N_4 has also been proposed as an interface layer for high K transition metal oxides since it has a higher K than SiO2 and is also an excellent diffusion barrier [4].

Thin amorphous silicon nitride dielectric layers have found many applications in great variety of electronic devices, including these as antireflective coating (ARC). Due to the large capture cross-section ratio (σn/σp = 100 at mid gap) of minority to majority charge carriers, passivation of the surface in p-type silicon is more crucial than in n-type silicon [5].

The surface stability of semiconductors plays a very important role in the fabrication of electronic devices. The formation of a insulator layer on Si by traditional ways of oxidation or deposition can not completely passivate the active dangling bonds at the semiconductor surface. Recently, nitridation of silicon films have been received much attention because silicon nitride film can suppress both of the leak current in insulating gate materials and interface reaction with metal oxide [5]. Thus, various non-traditional approaches for surface passivation such as ultra-thin sulphide, selenide layer or nitride formation have been a subject of increasing interest in recent years [6-17]. Also, the effect of nitride treatment is considered to be associated with passivation of the dangling bonds with nitride atoms and suppression of surface oxidation of Si. Detail of the Si and Si3N4 growth have been reported elsewhere [5,18-21]. However, it has been reported that the passivated surface of Si was quickly degraded when it was exposed to air ambient [20].

In this study, silicon nitride thin film has been deposited via electrochemical anodization on the Si(100) surface and non-aqueous ammonium polynitride ((NH4)2(NH2)x) electrolyte was employed to growth a silicon nitride layer on the Si surface as a new method for nitride passivation at the room temperature.

2. Experimental Procedure

In this study 2 inch diameter float zone (100) p-type (boron doped) single crystal silicon wafers having thickness of 280 μm with 0.8 Ωcm resistivity was used. The wafers were cleaved into 10x10 mm electrodes. The sample was ultrasonically cleaned in trichloroethylene and ethanol, etched by CP4 (HNO_3: HF: $COOHC_2H_5$: H_2O =3:1:2:2 weight ratio) solution for 30 s., rinsed by propylene glycol and blown with dry nitrogen gas. Ohmic contacts of the electrodes were formed by evaporating Al in high vacuum (P=10-6 Pa) and subsequently annealing them for a few minutes at 450 oC (for electrical measurement).

The nitridation set-up used in the study is the electrochemical anodization cell which consists of a p-Si anode and Pt as cathode, and is shown in Fig. 1. Agitation of the electrolyte is achieved by magnetic stirrer. Electrolyte used in the experiment was obtained by sequentially mixing of propylene glycol with ammonia (NH_3) and hydrazine (NH_2-NH_2) at 21:3:1 weight ratio, respectively. Preceding each cleaning step, the

wafer was rinsed thoroughly in de-ionized water of resistivity of 18 MΩcm.

Immediately after that, the substrate was immersed in electrolytical cell. Anodic nitridation was performed using a constant current source at different current densities, under N2 flow, in light and at room temperature (293 K). The potential difference between the electrodes normalised to calomel electrode was measured with an x-t recorder. The anodization was stopped when the cell voltage reached about the 18 V. Under constant current conditions, the nitride growth was followed by monitoring the voltage developed across the cell. With this monitoring it is possible to observe nucleation of nitride at the lower current density (0.1 mA/cm^2). After the nucleation phase in all of nitridation experiments, the behaviour of the cell voltage with time is linear, indicating the homogeneous composition of the grown nitride layers. After, the sample was immediately rinsed in propyl alcohol and blown with dry nitrogen and left in a desiccator.

For electrical measurements were formed by evaporating of Al dots with diameter of about 1.0 mm and 1500 Å thick in high vacuum (P=10-6 Pa).

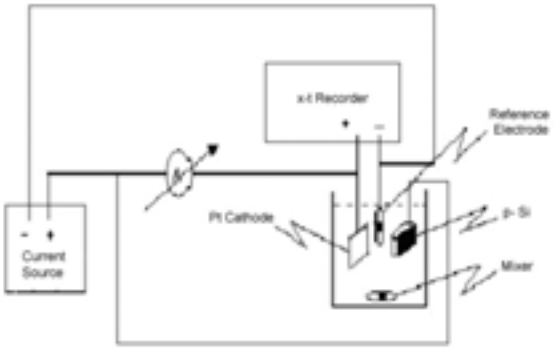

Figure 1. Non-aquenous anodic nitridation set-up

3. Results And Discussion

The Raman effect is an efficient way to determine the presence of pure silicon in its crystalline or amorphous form. Fig.2. shown that bulk crystalline silicon clearly exhibits a very thin band with a Raman shift at 520 cm^{-1} [22]. A peak from Raman spectrum for the very thin Si_3N_4 film was not detected.

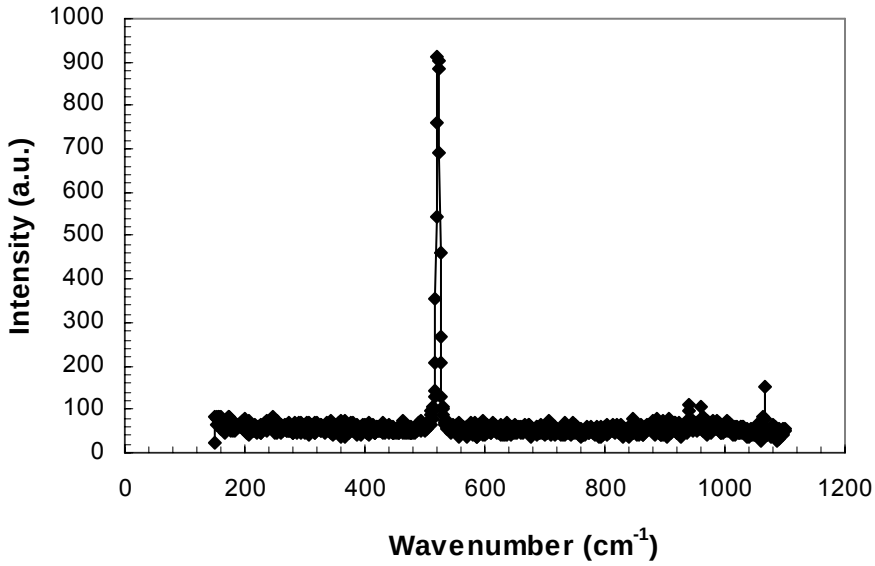

Figure 2. Raman spectra of the crystalline p type silicon

From these different experimental results in this study, several stages in the evolution of the structure and of the optical properties can be defined.

AFM were employed to characterize the surface morphology. Fig.3. shows the AFM micrograph of nitrided p-Si surface (without Al dot area on the film surface).

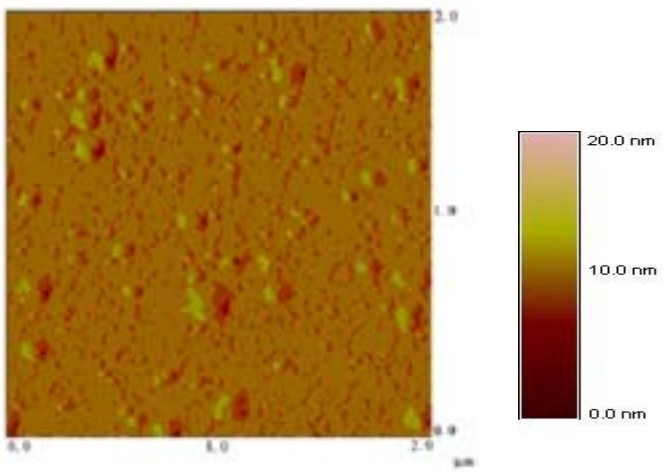

Figure 3. The AFM image of the Si_3N_4 deposited on the p-Si.

The root-mean-square (rms) surface rougness of these films obtained by AFM analysis (Fig. 3) indicates that the surface rougness is close to 0.6 nm. This value is very well for smooth surface.

X-ray diffraction (XRD) was used to assess the structure of the deposited Si3N4 layer. Our sample were formed by evaporating of Al dots with diameter of 1 mm (for electrical measurements). XRD diffraction indicates that information gives both the Al dot area and the without Al dot area on the film surface. Fig.4. indicates that surface of film are mixed phase of crystalline and amorphous structure.Thus, Si3N4 film is amorphous structure.

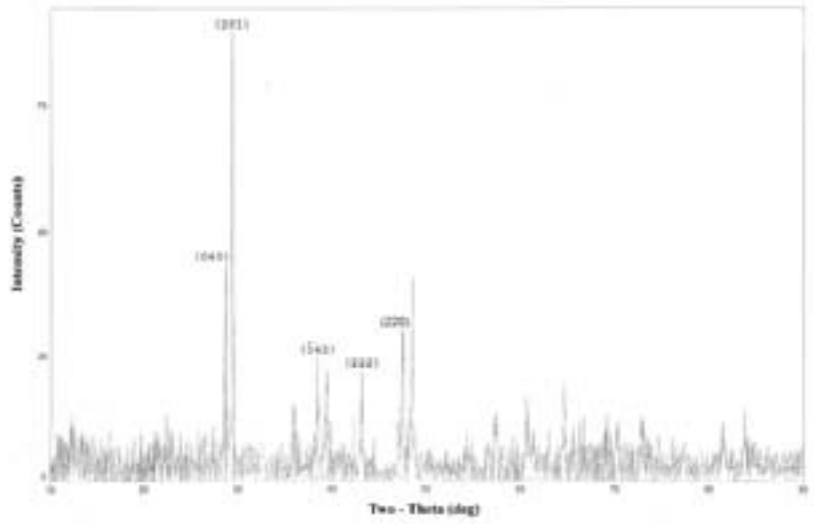

Figure 4. XRD spectrum which is obtained from surface Si_3N_4 degraded with air ambient and Al dot.

A sharp peak around 29º (2-theta) corresponds to a spacing of 3.0663 Å, which is related to the Si3Al6O12N2 (201) (Aluminum Silicon Oxide Nitride) detected from the Al dot. Two sharp peaks for SiO2 should be observed at the around 28 and 38º (2-theta) which correspond to (040) and ($\bar{1}$42) planes, respectively. The peak around 43º (2-theta) correspond to a spacing of 1.5187 Å, which is attributed to the N2O diffracted from (222) plane. The peak of Si3Al6O12N2 has been obtained from the Al dot. The peaks related to

SiO2 and N2O were obtained from the area which did not contain the Al dot. The peak at 47º (2-theta) is attributed to the substrate Si diffracted from (220) plane. There is no information about the peak at the around 48º (2-theta) peak.

The formation of the Si3Al6O12N2 structure was chemically analyzed. According to that reaction, Si3N4 was degraded by oxygen and Al dot. That was given in equation (1).

$$2Si_3Al_6O_{12}N_2 \rightarrow 6Al_2O_3 + 3SiO_2 + Si_3N_4 \quad (1)$$

Due to the degradation of Si3N4 with the air ambient, the compounds of SiO2 and N2O have been formed. That is also given in equation (2).

$$Si_3N_4 + 4O_2 \rightarrow 3SiO_2 + 2N_2O \quad (2)$$

Consequently, the stoichiometric Si3N4 on the Si(100) has been successfully produced.

4. Conclusion

The Si3N4 has been formed on the p-type Si(100) substrate thin film by using electrochemical anodization technique at the ambient temperature. Characterization of the thin film and Si were obtained Raman spectroscopy, AFM and XRD measurements. XRD pattern has shown the formation of stoichiometric Si3N4. AFM results show that the surface roughness of the Si3N4 film was about 0.6 nm. The surface roughness of the film is very important for the electronic devices. Thus, that value is quite good at performing a suitable thin film for electronic devices. It is concluded that the electrochemical anodization technique is an economical and practical way to produces a very thin film like the Si3N4 on the p-Si substrate.

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