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The Growth and Investigation of Interface of SiO_2/Si by Anodic Oxidation Technique Using Acetic Acid Medium

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ABSTRACT

This work investigats the physical properties and the nanotopography of the growth SiO_2 film in the thickness range (2.2- 12.9) nm on Silicon polycrystalline p-type substrates, by using the anodic oxidation technique using acetic acid medium containing 0.1N KNO_3 as supporting electrolyte. In this technique the polarization curve indicates the presence of active peak. The chemical analysis of the surface of SiO_2 has been done by (SEM) shows the presence of O_2 gas and C element, The films thickness has been found to increase as formation potential increases. The quality of the SiO_2/Si interface, as examined by FTIR and it appears, the value of band apbsorption displacement depends on SiO_2 thickness. Moreover the bond angle Si–O–Si has been found to depends on SiO_2 thickness. The (AFM) is used to study the nanotopography of SiO_2 film . However it has been found that a relation between SiO_2 film thickness and roughness of the SiO_2 film (As the SiO_2 thickness increase the surface roughness of SiO_2 film increase too).

Keywords : anodic oxidation, polarization curve, nanotopography of SiO_2 film.

استقصاء السطح البيني SiO_2/Si المنمى بطريقة تقنية الأكسدة الانودية باستخدام حامض الخليك

الملخص

يتضمن هذا العمل التحري عن الخواص الفيزياوية وطوبغرافية السطح النـانوي لغـشاء SiO_2 ذي سمك بحدود (2.2- 12.9) nm، والمنمى على أرضية سليكونية متعدد البلورات نوع p-type وذلك باستخدام تقنية الأكسدة الانودية وباستعمال محلول حامض الخليك بوجود 0.1N KNO_3 كاالكتروليت مساعد. في هذه التقنية تبين ظهور قمة التنشيط في منحني الاستقطاب. ولقد تبين مـن التحليـل الكيميـائي لـسطح SiO_2 باستخدام SEM بوجود غاز الأوكسجين (O_2)، وعنصر الكاربون (C). وكذلك لوحظ أن سـمك الاوكـسيد SiO_2 يزداد بزيادة جهد الإنماء. تم استخدام FTIR للتعرف على نوعية السطح البيني ل SiO_2/Si ولقد وجد إن قيمة كل من مقدار زحف حزمة الامتصاصية وزاوية الآصـرة(Si – O – Si) يعتمـدان علـى سـمك

الاوكسيد. وأخيرا تم استخدام تقنية AFM لدراسة طوبغرافية النانوية لغشاء SiO_2 ووجد أن هنالك علاقة بين سمك الاوكسيد ومعدل خشونة السطح إذ تزداد خشونة السطح مع زيادة سمك الاوكسيد.

INTRODUCTION

The Oxidation of silicon (Si) to produce thin and high quality oxide films is of scientific interest from a fundamental point view because of the many potential applications in the field of microelectronics such as photovoltaic cell and MEMS .The one most widely device used in silicon based integrated circuits is the MOSFET (Metal – Oxide – Semiconductor – Field – Effect – Transistor). The electrochemical oxidation technique (Anodic) is simple, fast and performed at room temperature in ambient conditions, as opposed to the long and sophisticated procedure to grow the oxide SiO_2 by using thermal oxidation technique (high temperature thermal oxidation of Si surfaces has been used for many years to produce silicon oxides). Moreover a potential advantage of the electrochemical technique over the thermal technique includes the precise control over the deposition rate at relatively low temperatures and low temperature processing is required to restrict doping impurity diffusion. Electrochemical technique for fabricating and modifying semiconductors have recently begun to show promise as practical substitutes for high vacuum techniques, as well as other known techniques. Recently then numerous studies have shown that anodic oxidation can produce thin and reproducible oxide layer on Silicon surface. Also electrochemical technique have been the source of information on the growth and surface morphologies of semiconductors. (Cristiano *et al*., 2008; Clark *et al*., 1994 ; Bardwell *et al*., 1995; Bardwell and Draper, 1996 ; Issa, 1999 ; Foll *et al*., 2002 ; Richard *et al*., 2003 ; Yahyaoui *et al*., 2004 ; Foca, *et al*., 2007; Issa, 2010).

In anodic oxidation technique the mechanical stresses at the border of the $Si\text{-}SiO_2$ structures are very small (Andrey, 2009). The interfacial stress is generated due to the volume expansion from Si to SiO_2 during the oxidation, and it is a strong function of growth conditions .The gate oxide thickness in nano fabrication of MOS devices are 20 A° or less. In this ultrathin film presence of a few defects or imperfections are limited .This defect will affect the SiO_2/Si interface stress , (Queeney *et al*., 2000 ; Queeney *et al*., 2004) .

To characterize the interfacial stress in a nano thin oxide films at the Si/SiO_2 interface , Fourier transform infrared spectroscopy (FTIR) technique was used. The absorption spectrum gives the information for this through the positions of absorption frequency peaks of Si–O–Si bonds in SiO. Higher stress is associated with a denser oxide film, smaller Si–O–Si bond angle and lower peak. The electrochemical oxidation technique may offer a variety of possibilities to control the interface properties (Queeney *et al*., 2004 ; Min-Soo *et al.,* 1999 Tien-Chun and Krishna, 2000). The nanotechnology plays an important role for the fabrication of the electronic devices in this day. Therefore, in order to create new devices and structural properties and thus new functionality, novel micro- and nanotopographies are must be aimed (Empestl *et al*., 2008).

Recently, nanotopography of the surface of silicon wafers has been an important issue because it gives information about the uniformity of the thickness variation of dielectrics. (Queeney *et al*., 2004). It is of critical importance nowadays for both silicon wafer venders and device manufacturers to understand how the various characters of the

nanotopography of wafers impact on oxide. (Katoh *et al*., 2002). For high resolution surface investigations, the AFM technique used. This technique resolves surface structure down to the nanometer scale. AFM consists of scanning a sharp tip on the end of a flexible cantilever across a sample surface while maintaining a small, constant force. In addition, there is a strong anisotropy in anodic oxidation For applications in micro-electromechanical systems (MEMS). (Nakhei and Bahari, 2009 ; Philipsen, 2007).

This work firstly involves the growth of nano-thickness film of SiO_2 on silicon p-type polycrystalline in acetic acid medium by using anodic oxidation technique. Secondly the investigation of interface SiO_2/Si by using Fourier transform infrared spectroscopy (FTIR), the chemical analyses of SiO_2 surface by using scanning electron microscope (SEM) and nanotopgraphy of SiO_2 film by using Atomic force microscopy (AFM) has been done.

EXPERIMENT

The wafers used is p-type polycrystalline silicon (1-5) Ω. cm. Before the sample was oxidized, it was first degreased by rinsing in acetone, Isopropanol, methanol and finally dionized water.The native oxide was removed by etching in 1% HF for 1 min. The SiO_2 films were grown at constant potential using Potentiostat (Wenking, HP 72, Germany) (1-15) V in which three electrodes cell were used: a (1X1) cm Silicon wafer as a working first electrode, the second was the reference electrode is Saturated Calmel Electrode (SCE), and the third counter electrode is Pt. The electrolytic mediumused in acetic acid containing 0.1N KNO_3 as supporting electrolyte. The polarization curve was studied using the Scanning potentiometer (Wenking, Bank, SMP72, Germany). To characterize the interfacial stress FTIR (BRUKER TENSOR 27) technique was used. Oxide thickness was measured by Ellipsometer (J. A. Wodllam V.VASE). The Scanning Electron Microscope SEM (EDAX-Genesis) was used to analyse present elements in the sample. Atomic Force Microscopy AFM MODEL PSIA (XE-100E) was used to analyse the surface nanotopography .

RESULTS AND DISCUSSION

This section involve the results and discussion of growth nano SiO_2 thin film on p-type polycrystalline Silicon wafer, the relation between oxide thickness and formation potential, surface chemical analysis by using SEM the interfacial stress by using FTIR and finally the nanotopography by using AFM.

Polarization Curve

The electrochemical polarization curve of silicon in acetic acid medium containing 0.1N KNO_3 as supporting electrolyte is shown in Fig. (1). the active peak is appeared at 2 volt in the polarization curve, The shape and place of active peak in polarization curve depends on change of interface energy level between the medium and substrate . Moreover the current increases with increasing applied potential and break at 14 volte. This is due to the generation oxygen at surface of electrode .This results was found in good agreement with results (Foll *et al*., 2002 ; Issa, 2010 ; Philipsen, 2007).

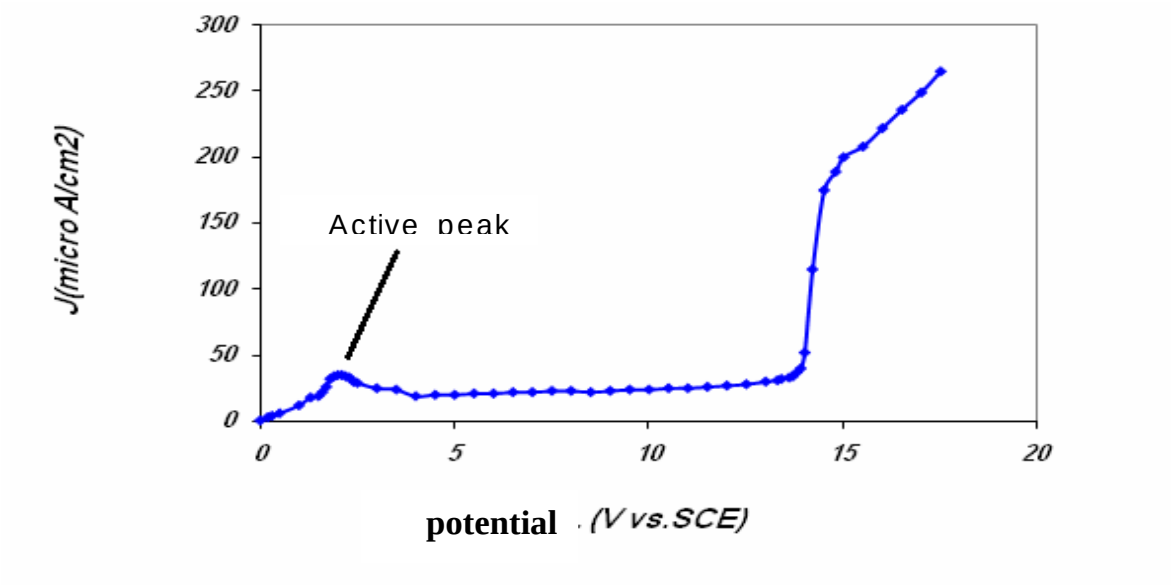

Fig. 1: Electrochemical polarization curve for P-type polycrystalline silicon in acetic acid medium.The ramp rate was 10 mV/sec

The relation between oxide thickness and formation potential

The relation between oxide thickness and formation potential is shown in Fig. (2). It is very clear that the formed oxide increases with increasing formation potential and the relation between them is found to be semi liner up to (8.8 nm) and discontinues above thickness (8.8 nm). This agree with the results obtained by (Bardwell *et al.*, 1995 ; Bardwell and Draper, 1996 ; Clark *et al.*, 1994).

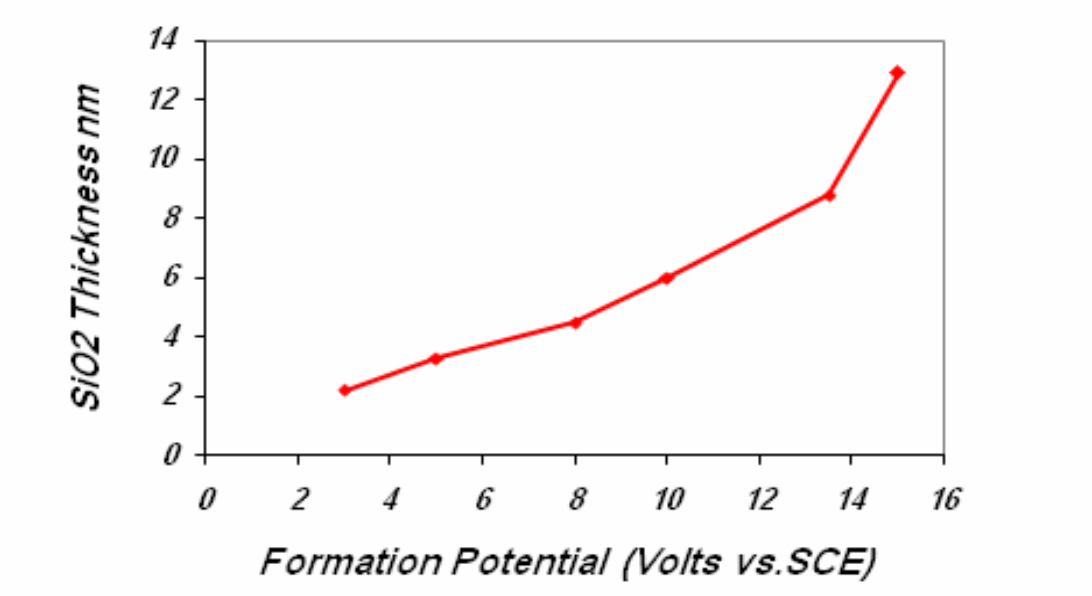

Fig. 2: Relationship between the formation potential and the thickness of SiO_2 growth on p-type polycrystalline Silicon.

Chemical analysis of SiO2 surface using (SEM)

The chemical analysis of the surface of SiO_2 grown on the surface of silicon polycrystalline P-type has been done by (SEM), which shows the presence of O and C elements as shown in the Fig. (3).The carbon that appeared in this figure come from acetic acid medium during oxidation. This agree with the results obtained by (Issa, 2010).

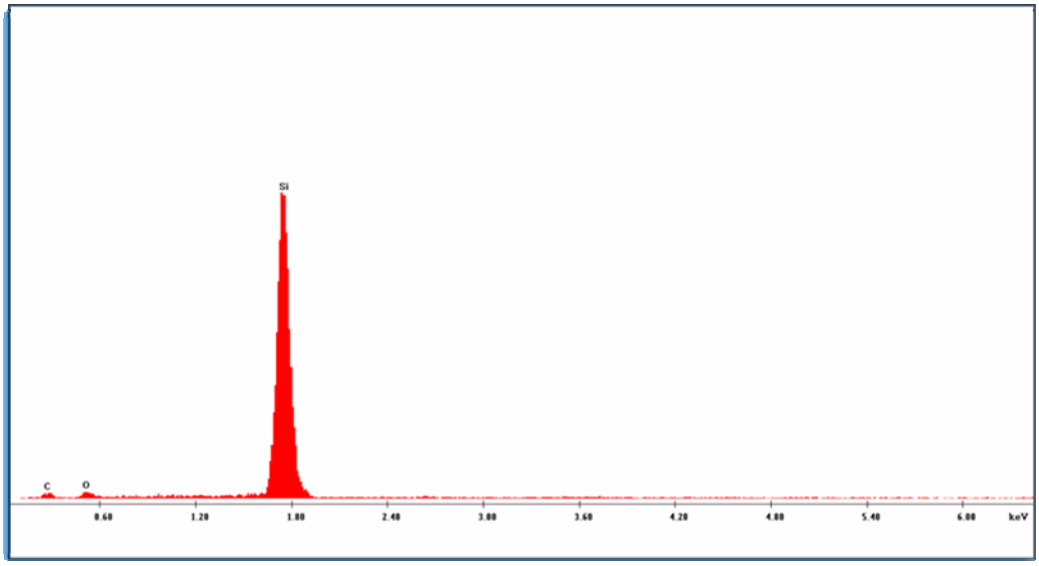

Fig. 3: Chemical analysis using (SEM) of the surface of SiO_2 growth on the surface of p-type polycrystalline silicon.

FTIR Spectrum

Fig. (4) showed the FTIR spectrum of SiO_2 grown on p-type polycrystalline silicon. substrate. This Fig. shows astrentching band at wave number (1107.26 cm^{-1}), bending band wave number (816.68 cm^{-1}) and roching band (514.18 $cm^{-}1$). This agree with the results obtained by (Issa, 2010 ; Barbara, 2004).

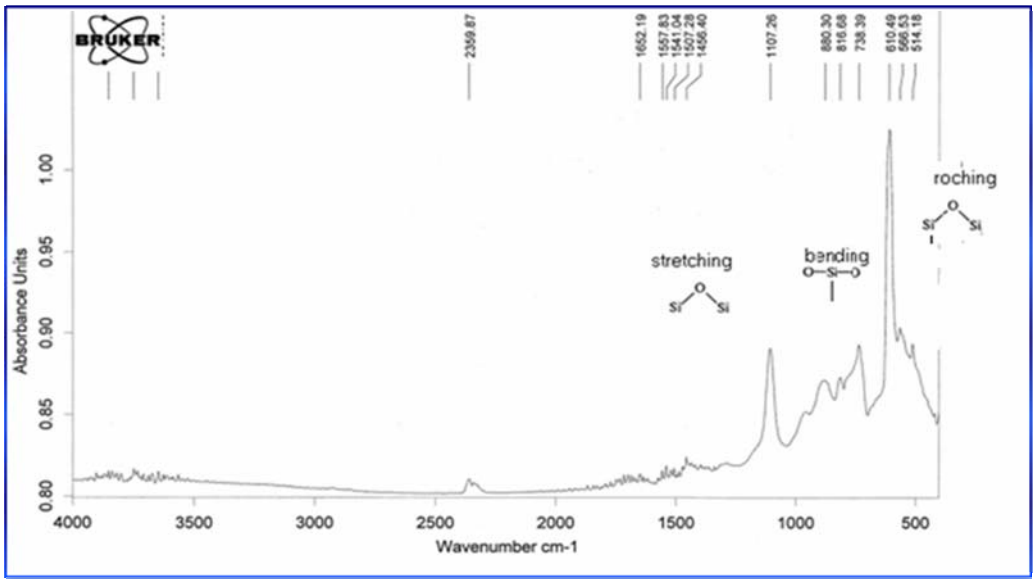

Fig. 4: FTIR Spectrum for SiO_2 growth on p-type polycrystalline silicon.

Fig. (5) showed that the relationship between the stretching frequency absorbance band and thickness of SiO_2 growth on P-type polycrystalline silicon substrate. From this Fig. one can see the stretching frequency band shifts toward the shorter wavelength number with increasing thickness of the SiO_2. This may be due to the stress at the Si/SiO_2 interface. When the SiO_2 thickness increases the stress may be generated by the entry of oxygen atoms in the lattice of Silicon. The process leads to change in crystal size and then increases the pressure inside the crystal. However, this change will affects on the Si/SiO2 interface (Zhenrui *et al.,* 2006).

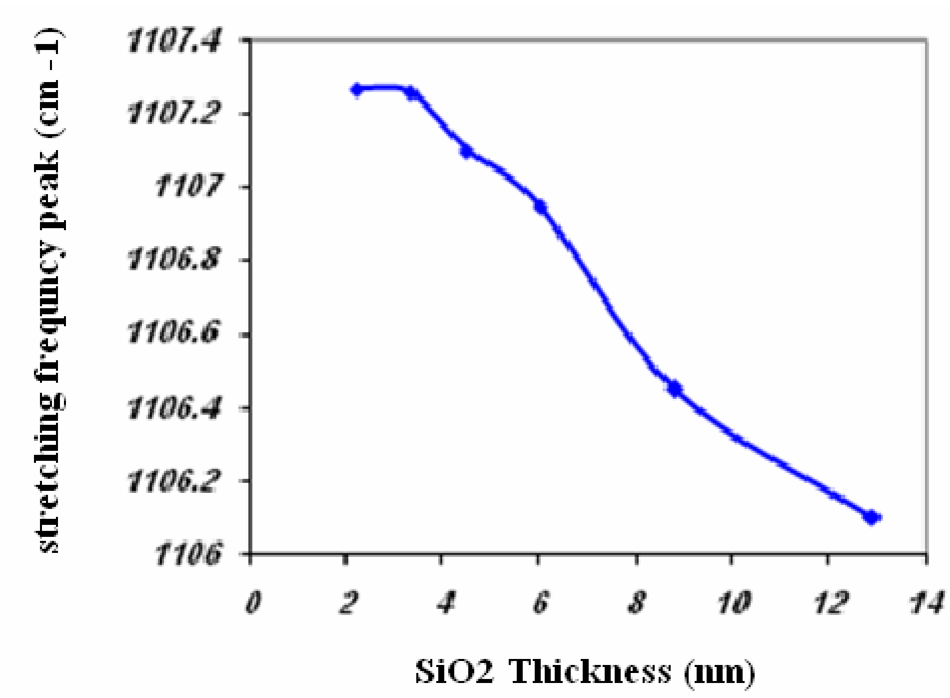

Fig. 5: Relationship between the stretching frequency absorbance band and thickness of SiO_2 growth on p-type polycrystalline Silicon.

Fig (6) shows the relationship between angle Si-O-Si and the thickness of SiO_2 growth on p-type polycrystalline silicon substrate can see the increasing SiO_2 thickness the Si-O-Si angle decreases in magnitude. However the angle Si-O-Si was calculated by equation (1). (Nakamura and Ichimura, 2005 ; Tien-Chun and Krishna, 2000).

$$\nu = \nu_{\circ} \sin \Theta/2 \qquad \text{(1)}$$

Where ν is the peak of the absorption frequency (stretching frequency), $\nu_{\circ}$ =1134 cm^{-1} and Θ angle of bond Si-O-Si

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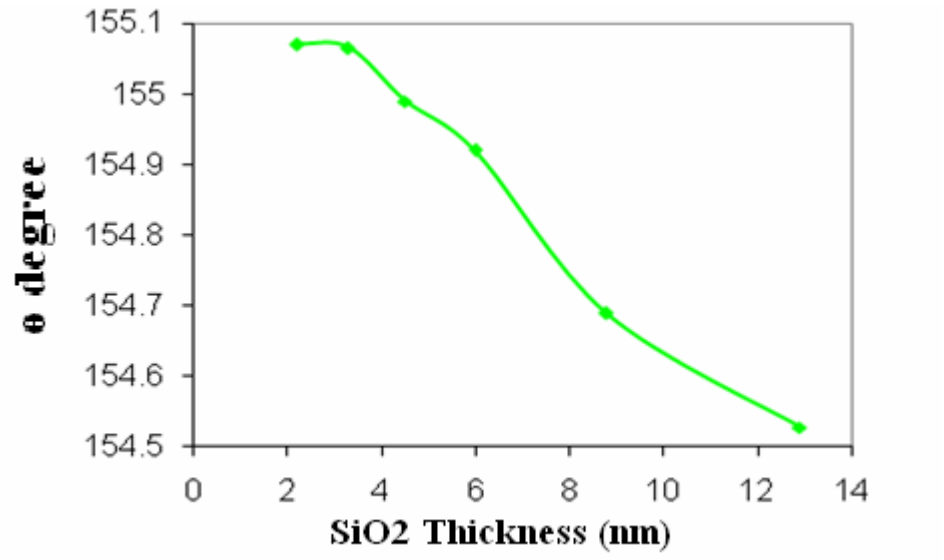

Fig. 6: Relationship between angle Si-O-Si and the thickness of SiO2 growth on p-type polycrystalline silicon.

AFM Measurement

Atomic force microscopy was used to investigate the corresponding structural properties of SiO_2 surface growth by anodic oxidation in acetic acid medium. The nanotopographical AFM images of SiO_2 surface growth on silicon polycrystalline are shown in Fig. (7). The study of the relation SiO_2 film nanotopography growth on silicon polycrystalline with SiO_2 thickness shows in Fig. (8). From this figure the relation is liner and the root mean square roughness of the surface SiO_2 increases with the increases of SiO_2 thickness.

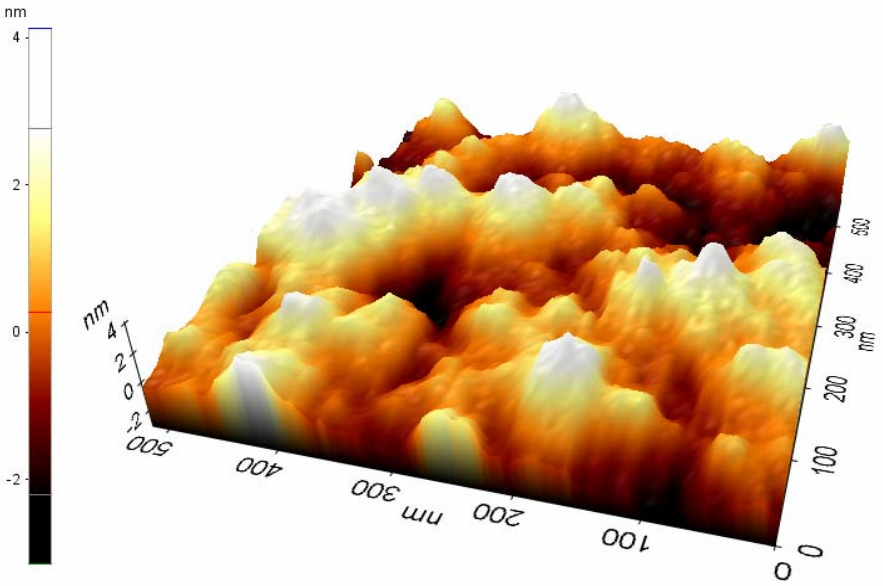

Fig.7:The nanotopography AFM images of SiO_2 surface growth on p-type polycrystalline silicon.

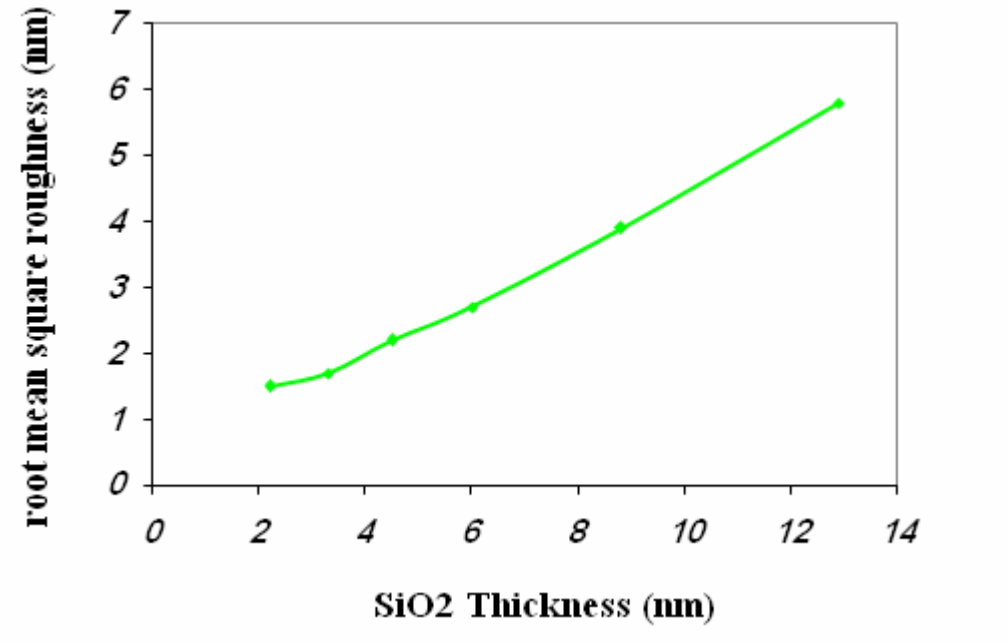

Fig. 8: Relation between the root mean square roughness (measured by AFM) with thickness of the SiO_2.

CONCLUSIONS

In polarization curves of silicon in acetic acid medium containing 0.1N KNO_3 as supporting electrolyte an active peak appeared . SiO_2 electrochemical deposited on silicon polycrystalline were at nano scale (2.2- 12.9) nm. and the relation between oxide thickness and formation potential is semi liner up to (8.8 nm) and breaks above thickness (8.8nm).

The chemical analysis of the surface of SiO_2 has been done by (SEM) show the presence of O and C elements.

From FTIR spectrum stretching frequency band shifts toward the shorter wave number with increasing thickness of the SiO_2. Also increasing SiO_2 thickness, the Si-O-Si angle decreases in magnitude.

AFM was used to analyzed nanotopography surface of SiO_2. The results clearly showed a quantitative relationship between the nanotopography and the film thickness variation. The relation between SiO_2 film topography and SiO_2 thickness is liner. These analyses are very useful techniques to interpret the quantitative relationship between the nanotopography and the oxide characteristics.

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