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Comparison of stress, strain, and elastic properties for porous silicon layers supported by substrate and corresponding membranes

R.S. Dariani*, M. Nazari

Department of Physics, Alzahra University, Tehran, 1993893973, Iran

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ABSTRACT

This paper describes characterization of mechanical properties of porous silicon (PS) layers with different porosities using high resolution XRD. The XRD measurement determined various mechanical properties of PS such as; Young modulus, Poisson's ratio, and lattice parameter expansion. Our results indicated that mechanical properties reduce with increasing porosity. Also, the mechanical properties of two different porous layers, either supported by or detached from the substrate were examined. Comparison of the two porous layers showed that the constraint in the interatomic spacing is the origin of the lattice constant expansion in the planes perpendicular to the surface. This phenomenon can be useful for gas sensor applications.

1. Introduction

Recently, porous silicon (PS) has been received many attentions, due to its unique and outstanding structural, optical, and electrical properties have attracted attention for a great variety of applications such as; delivery of the antibacterial drug triclosan [1], dye-sensitized solar cells [2], photocatalysis [3], various cleaning devices [4], anti-fog windows, and vivo sensing applications due to its biocompatibility [5]. On the other hand, XRD measurements showed that the lattice constant of PS is expanded in the direction perpendicular to the sample surface because of the lattice mismatch at interface between the Si substrate and PS film, the unit cell of PS is tetragonally distorted and the film is strained [6]. The lattice mismatch is expected to introduce stress field around an edge dislocation at the interface [7,8]. Most of applications in PS nanostructures have been focused on exploiting electrical and optical properties. However, a few researches have been reported on the mechanical properties of PS, such as Young's modulus and Poisson's ratio. The Young's modulus of PS has been investigated using XRD diffraction, acoustic wave propagation and nano-indentation technique [9]. Studying the elastic properties of PS can help to realize the cracking phenomenon shown on PS samples in high porosity during drying after anodization process [10].

The residual stress in thin films is almost determined from the substrate curvature [11], X-ray diffraction [12], or Raman spectroscopy [13]. It is well known that the residual stress affects not only on the mechanical properties, crack resistibility, and durability of the material but also on chemical reactivity and other physical properties due to deformation of the crystal structure. The residual stress of the films is an important property for applications in industry due to balance of internal stress and adherence of the films dominates peeling durability of the films [14].

Optimization of the mechanical properties of PS layers as well as stress control is an important issue that has to be considered for most of these applications [15]. Characterization of the Young's modulus also allows to accurately design and optimize the modeling of mechanical structures that could be potentially built from PS. Barla et al. [16] believed that lattice expansion is due to size effect; meanwhile the other group [17] thought it is due to the presence of SiO_2, even for fresh samples. However, researchers suggest that for clean Si surface the average intrinsic surface stress tensor is likely positive, so small Si particles should have a lattice parameter contraction [18]. However, electrochemically fabricated PS does not have a clean surface and often the lattice parameter expansion has been attributed to the influence of chemisorbed SiH_x hydrogen groups at Si surface [19]. Si during etching process shows structure similar to sponges with Si pillars and pores covered by hydrogen [20].

In this paper, the mechanical properties of PS such as; Young's modulus, Poisson's ratio, lattice parameter expansion, and stress

* Corresponding author.
E-mail address: dariani@alzahra.ac.ir (R.S. Dariani).

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were obtained by X-ray diffraction experiments for different porosities. X-ray rocking curves provided the stress at the interface and gave the lattice mismatch. This is the first time that the lattice parameter and elastic property for different porosities is reported for low doped p-type PS samples. Also, we studied the mechanical properties of two different porous layers, either supported by or detached from the substrate and comparison of mechanical properties is done for the supported porous layer with pores closed at one end and for membrane layers with pores open at both ends. It will also be seen that the findings in this paper relying solely on high resolution XRD data when investigating the nature of lattice distortions.

2. Experimental details

PS samples were fabricated from p-type Si wafer with boron doped, (100) orientation, 1–5 Ω-cm resistivity, and 525 μm thickness. Si wafers were cleaned by acetone, ethanol, and distilled water; respectively to remove dirty and dust. For ohmic contact, back side of Si wafer were coated with 1 μm thickness of Al (99% pure) at 10^{-5} mbar vacuum. Then, samples were annealed in a furnace at 400 °C for 30 min with heating rate of 20 °C/min. Si wafer was connected to anode and Pt to cathode in an electrochemical Teflon cell. Si wafer was parallel to Pt and distance between them was 1 cm. Anodization parameters were as following: electrolyte solution of 40% HF and ethanol with volume ratio of 1:1, current density of 20 mA/cm^2, and etching times of 10, 20, 30, and 40 min. After etching, the samples were rinsed in ethanol and blown dried by air. In Table 1, variation of the etching time leads to change the porosity of samples. At constant current density of 20 mA/cm^2 one expects almost constant pore diameter. Porosity and pore diameter of our samples were measured with Microstructure Measurement software from FESEM images which were taken by ZEISS Co. system, AMA model. Porosities were measured by averaging 50 points which were taken by Microstructure Measurement software from FESEM images. Also, porosities of our samples were checked by gravimetric method. The porosity results which were taken from software and gravimetric method convinced us that our porosities are reliable. Our samples showed homogenies structures. The thickness of porous layer increases with increasing the etching time however, pore diameter is almost constant when other parameters such as current density and HF concentration are kept constant. In this work, PS surface is fairly uniform with pore diameter of 14 nm. Longer etching time means that Si stays in HF solution for a longer time and so the mass of dissolved silicon (the porous layer) in HF solution become larger [21,22]. Therefore, increasing porosity with increasing etching time is due to increasing number of pores. The present data are in agreement with the general trend of increasing porosity with increasing etching time that has been widely reported [26–23].

X'pert pro MPD, PANalytical system was used for omega scan and rotational scan with monochromatic CuKα1 radiation (λ = 1.54060 Å) source. Angel resolution (error bar) for determination of Bragg angle was 0.02° and for omega scan was 0.005°. The XRD system is operated in the high resolution mode. This mode has the advantage of being able to distinguish between strain induced lattice mismatch (reported by θ–2θ scan) and layer tilt or misorientation (reported by rocking curve).

Table 1
The fabricated samples characteristics.

Sample no.	Current density (mA/cm^2)	Etching time (min)	Porosity (%)
PS1	20	10	20
PS2	20	20	33
PS3	20	30	38
PS4	20	40	40

3. Results and discussions

3.1. Mechanical properties

XRD method is a non-destructive method for measuring residual stress. This method is used for determination of stress from distance variations between crystal planes named strain. According to Bragg law, resolution at distance between crystal planes is related to determination of diffraction curve peak position. In XRD with normal resolution only one peak is seen for PS samples which are standing on Si substrate, which means PS lattice parameter mean is similar to Si without any expansion and contraction. Meanwhile, high resolution XRD shows that the PS samples have two distinct peaks, one obvious peak which is main peak and another small one which is on shoulder (Fig. 1a). The main peak did not show any different orientation with its substrate, since X-ray diffraction experiments were performed at the (400) reflection from the lattice planes parallel to the (100) Si surface. The shoulder peak is related to loose layer which is belongs to PS itself and have lower diffraction angle. This peak is due to lattice expansion of z direction since axial stress is in x–y plane. For most samples, porosity creates single wide peak. Also other researches show that porous layer have similar lattice with substrate at x–y plane [13].

Table 2 shows that for PS samples with increasing porosity and etching time, PS diffraction angle (θ_{PS}) reduces due to displacement of lattice planes and producing perpendicular strain. This angle reduction in samples causes lattice expansion enhancement, Δθ is angle displacement between PS and Si peaks ($\Delta\theta = \theta_{PS} - \theta_{Si}$). This displacement shows that porous layer lattice parameter at perpendicular direction increases and according to Eq. (3), expansion strain causes peak displacement toward low angles.

According to M. Karim et al. [27] the PS peak is at a lower angle relative to the Si reference peak. This is the case for all the as-etched samples but with different angular splitting Δθ between the two peaks. This splitting between the two peaks increases as the thickness of the monolayer of PS increases from 350 to 1700 nm. This indicates an increase in the expansion of the PS lattice in the normal direction to the Si substrate, implying a ~26% incremental increase in the out-of-plane tensile strain from 3.5×10^{-4} to 4.6×10^{-4}.

Strain in a crystal determines using Bragg equation when d is lattice interplanar distance (d spacing), at strain manner the plane distance varies as Δd due to Bragg equation, differential of Bragg equation at constant wavelength is resulting approximately strain equation as following [28].

$$n\lambda = 2d\sin\theta \tag{1}$$

$$0 = 2\ \Delta d\sin\theta + 2d\cos\theta\ d\theta \tag{2}$$

$$(\Delta d/d)_{\perp} = -(\Delta\theta/\tan\theta) \tag{3}$$

On the other hand, lattice expansion equation (Eq. (4)) is the same with equation obtained from Bragg law for strain [29]:

$$(\Delta a/a)_{\perp} = -(\Delta\omega/\tan\theta) \tag{4}$$

Rocking curve also can determine samples offset. Generally, surface topographic shape of every sample has a decline and this offset can be positive, negative, or zero. We have controlled our samples parameters to get zero for our samples' offset. Detector is kept constant for measuring rocking curve and then diffraction