Porous Silicon/SiCN Pedestal Cantilever Biosensors

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Abstract

Silicon-based cantilever biosensors used for the characterization of physical properties of cells such as their mass and stiffness have been gaining great interest and have profound implications in cell biology, tissue engineering, cancer, and disease research. The electrochemically made porous silicon (PSi) has been promising in terms of immobilizing biological molecules through its porosity and has led to improved biosensing applications. However, PSi loses its mechanical strength with porosity. The one-end cantilever sensors on the other hand are subject to non-uniform mass sensitivity. A novel SiCN and PSi-based pedestal cantilever structure have therefore been proposed which can result in improved biosensing. Nanoindentation of SiCN films showed the mechanical strength whereas Finite Element modeling was done to show mass homogeneity for the system.

Keywords: Biosensors, Porous Si, SiCN, cantilever, nanoindentation, Finite element modeling

1. Introduction

The conjunction between optical and mechanical properties in silicon has given rise to some significant applications, the most coveted of them is in the field of biosensing. Optical cantilever sensors find their use in Atomic Force microscopes and other related surface characterization techniques[1]. Piezo cantilevers on CMOS photonic platform have been used for sensing technologies. Mach Zehnder interferometers (MZI) have been used to study light interaction with molecular[2]. Porous silicon, which is an electrochemical derivative of silicon has been used as a biosensor. It is bio-compatible and can hold the biological materials inside its pore causing immobilization of the sample during tests and hence leading to enhancement of sensitivity[3-6]. The electrical properties like conductivity as well as the optical properties like refractive index show commendable changes when foreign molecules get attached to it. The porosity % on which the whole sensing capability of PSi is based can be tuned by the etching parameters like current density and etch time[7]. This communication however focuses on the PSi-based cantilever structures used for biosensing and hence the mechanical aspects of PSi-based structure have also been discussed

The mechanical stability of PS used as a cantilever studied by nanoindentation however showed a decrease in H and E values due to an increase in porosity[8, 9]. Thin films of suitable materials deposited on silicon before the etching process involving proper fabrication can lead to the formation of stable PSi-based cantilever structures applicable to sensing. The cantilever-based MEMS resonator sensors on the other hand suffer the problem of un attainment of homogenous mass sensitivity. The intensity of vibration being highest at the free end of the cantilever makes the mass sensitivity highest and a reduction as one moves towards the fixed end. The resonant frequency of operation is inversely proportional to the mass may hamper the sensing efficiency[10]. This communication, therefore, analyses a previously proposed pedestal cantilever structure and suggests a novel SiCN and PSi-based cantilever foundation for biosensing.

The ternary nanocomposite material Si-C-N was first introduced to the scientific community as a high-temperature oxidation-resistant polymer-derived ceramic (PDCs) [11]. PDCs are a new class of ceramics that combines the functional properties of polymers with the mechanical and chemical durability of ceramics. Polymer-derived ceramics (PDCs) have a polymer-like nanostructure and ceramic-like properties, e.g., creep and oxidation resistance [12].

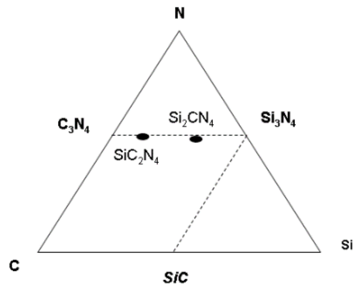

Fig 1. Ternary phase diagram of Si-C-N

Apart from high-temperature oxidation resistance, the hardness as well as high-temperature stability of the Si–N–C phase exceeds those of SiC and Si_3N_4. The electronic band gap of 2.5-3.8 eV allows us to consider this material as a wide band gap and dielectric material. More importantly, stability of β-C_3N_4 with comparable diamond hardness has been achieved in ternary silicon carbonitride. The Si-C-N phase diagram is shown in **Fig 1**. The incorporation of Si in the CN deposit promotes the inclusion of nitrogen and leads to C_3N_4. The Si-C-N has shown stability up to 1600°C and it remains in the amorphous state up to 1500°C.These properties make silicon carbonitride a promising material for prospective applications such as structural ceramics, MEMS, hard protective coatings, and electronic materials [12-17].

2. Materials and Methods

There is a standard method of forming adopted by researchers with slight alterations[18, 19]. PSi is usually made in an electrochemical bath consisting of HF as an electrolyte. The P-type Si wafer (100) having a 3.14 cm^2 area with a resistivity of 1 to 2 Ωcm were anodized in the formation bath. The wafers act as a seal between the front and rear region of the formation bath. The front region was filled with HF: C_3H_7OH in a 1: 1 ratio while the rear portion was immersed in KCl solution. The silicon chip which gets etched away is used as an anode while graphite rods are used as cathode. The graphite rods in turn are kept in a KCl solution for conductivity. The current used, concentration of the electrolyte, the resistivity of the silicon chip, and the time for which the reaction takes place are considered to be the etching parameters. The variation of etching parameters and luminescence properties of PSi have been reported earlier [20].

The SiCN nanocomposite hard coatings were deposited on Si by magnetron sputtering. A 2-inch dia sintered SiC pellet was used as the target. Argon followed by nitrogen gas were introduced in an evacuated chamber for the reactive sputtering process the details of which along with the microstructural as well as structural characterizations have been reported [21, 22].

Nanoindentation is often used in studying the mechanical properties of thin films deposited on Si applicable for sensing purposes. It has also been recently reported to be used for finding the stiffness of soft biomaterials and organs.[23] It is a method to characterize material mechanical properties on a very small scale due to its high spatial and depth resolution of the measurement., the details of which can be found elsewhere.[24-26]

3. Results and discussions

In a single layer of porous silicon, pores of varied dimensions can be observed due to non-uniform etching caused by unevenness of the sample. These pores are responsible for the immobilization of the biological molecules and are helpful for sensors. A variation in etching parameters is related to the porosity which is crucial for gas sensing capabilities. However, PS is losing mechanical strength with porosity. A mechanically stable structure is very much required for MEMS cantilever sensors.

Although Silicon is the preferred choice for piezoresistive sensors due to controllable/repeatable properties and well-established processing techniques. Silicon-based MEMS sensors operate reliably only up to a temperature of about 150 °C[27] Therefore, for high temperatures, SiC stands out as one of the most promising candidates[28]. An up-gradation of SiC comes in the form of SiCN which can withstand even higher temperatures than SiC. Phases like SiNx (including) β-Si_3N_4) and CNx (including β-C_3N_4) are formed in the nanocomposite SiCN thin film providing good thermomechanical and conducting properties.

Nanoindentation showed hardness of 20 GPa and Modulus of 240 GPa for the SiCN films which are quite impressive considering the sharp Berkovich indenter. The substrate effect usually starts when the penetration crosses a depth that is 1/10th of the film thickness. Considering this the film thickness can be estimated to be 300 nm approximately (**Fig 2b**). The load-depth plot in **Fig 2a** shows that a 1.8 mN load was required by the indenter to reach a depth close to 80 nm. The parameters h_r, h_e, h_t, h_c, and h_a are the residual elastic total contact depth and sink in-depth respectively[27, 28].

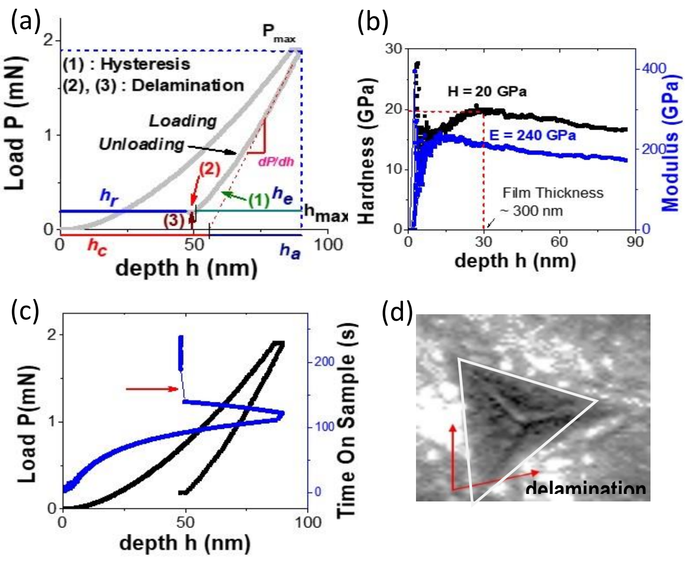

Fig 2. Nanoindentation a) Load-depth plot and b) Hardness-Modulus plot for SiCN films on silicon substrate c) Load and Time on the sample and (d) optical image of the nanoindentation impression

The deviation from linearity as observed in the unloading portion is called the hysteresis effect) indicated as 1 in the figure). The linear region parallel to the depth (indicated as 2) and the nonattainment of 0 N after full unloading (indicated as 3) is due to the partial delamination of the film as also observed in the optical image of the nanoindentation region, the shape of which has been marked arising from 3 sided pyramidal Berkovich indenter. The bright regions surrounding the indentation confirmed the partial delamination from the sides of the indenter impression (**Fig 2d**). The delaminated regions have higher brightness as they are closer to the lens. The time on the sample plot also indicated the delamination upon loading as a vertical spike was observed without any load changes (**Fig 2c**).

Silicon Carbon nitride (Si-C-N) thin films have an application in high-temperature pressure sensors due to their piezoresistive properties[28]. The properties of SiCN applicable to MEMS piezoresistive devices are given in Table 1 [29-33]. Therefore, a combined structure of SiCN and Porous Silicon as discussed below (**Fig 3**) where the Si substrate is coated with SiCN film first followed by etching taking place will have the property of cantilever biosensors at the same time will be mechanically stable.

Table 1. Parameters of SiCN useful for piezoresistive applications

Parameter	Value
Bandgap	2.3–3.0 eV
Break down voltage	29 V at RT with leakage current density 1.2×10^{-4} A/cm^2
	5 V at 200oC 1.47×10^{-4} A/cm^2
Modulus	240 GPa
Chemical inertness	excellent
MEMS compatibility	excellent

The PSi layer is clamped at the four pedestals made of SiCN as seen in the top view (**Fig 3b**) and is subject to vibrations on trapping biomolecules in its pores as shown in the cross-sectional view (**Fig 3 a**). Therefore, this new cantilever design can overcome the non-uniform mass sensitivity associated with one-end cantilevers.

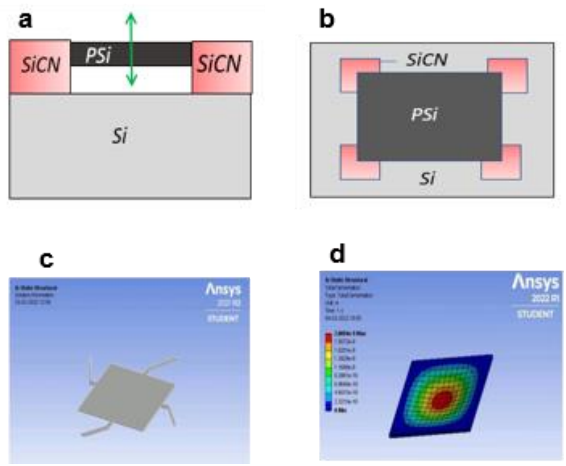

Fig 3. SiCN and PSi-based cantilever for biosensing (a) cross-sectional and (b) Top view (c) Cantilever with pedestal geometry[9] and its (d) FEM analysis.

Because the resonant frequency of the sensor is inversely proportional to the square root of its total mass measurement of resonant frequency shift between the system with and without the target mass gives the mass of the target entity. Using these unique characteristics of the MEMS-based sensor, various physical quantities, such as mass, stiffness, viscosity, and so on, have been measured: one of the commonly measured entities is the biological cells. The characterization of physical properties of cells such as their mass and stiffness has been gaining great interest and can have profound implications in cell biology, tissue engineering, cancer, and disease research. However, it is commonly known that the Cantilever-type resonator has a non-uniform mass sensitivity that significantly changes based on the locations where the target is attached: the mass sensitivity is at its maximum when theadded mass is placed at the free end of the cantilever and the sensitivity decreases to zero asthe added mass gets to the fixed end of the cantilever. In other words, the measured mass reading is a function of the location of the cell relative to the free end that determines the mass that is measured.

A novel design with pedestal geometry has been proposed which can solve this non-uniform mass sensitivity as given in **Fig 3(c)**.[9] Finite element modeling showing the stress distribution concerning time for total deformation is shown in **Fig 3(d)**. It is observed that the structure is most sensitive at the canter which shows uniform reduction on moving towards the edges. Hence the cantilever structure as proposed, which is quite similar to the pedestal cantilever, will not have the problem of non-uniform mass sensitivity.

4. Conclusions

The mechanical instability associated with porous silicon due to an increase in porosity and the non-uniform mass sensitivity associated with single clamped cantilevers were addressed and a novel cantilever biosensor based on SiCN hard coatings and PSi was proposed. The growth of PSi concerning etching parameters and Nanoindentation of SiCN films deposited on Si showed hardness of 20 GPa and Modulus of 240 GPa. Finite element analysis of a pedestal cantilever was done which showed the stress distribution with a central maximum radially decreasing towards the edges. Hence the proposed structure was found to be free from non-uniform mass sensitivity and also a mechanically stable system.

DECLARATIONS

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of competing Interest

The authors declare no conflict of interest

Ethics approval

The submitted work is original and has not been published elsewhere in any form or language

Availability of data and materials

Available on request

Disclosure of potential conflicts of interest

There is no potential conflict of interest

Acknowledgments

The authors would like to thank Dr. S.M. Hossain IIEST, Howrah for his valuable guidance and Dr. S. K. Mishra, CSIR-National Metallurgical Laboratory, for experimental facilities.

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