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# Hydrogen-ion implantation effect on $SiO_2$-matrix B-doped Si-NC thin films with improved conductivity

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ABSTRACT

In this work, the $SiO_2$-matrix B-doped Si-NC (BDS) thin films have been modified by hydrogen-ion implantation to improve their conductivity. The effects of hydrogen-ion energy on the structural and electrical properties of Si-NC thin films were investigated systematically using photoluminescence, X-ray photoelectron spectroscope and Hall measurements. Results showed that the order of the thin-film surface structure was perfected, the defect density and resistivity were both firstly reduced and then increased when the hydrogen-ion energy was increased from 0 eV to 500 eV. The BDS thin films passivated with hydrogen-ion implantation of 100 eV exhibited the lowest resistivity. The change in micro-structure and resistivity of the BDS thin films probably resulted from hydrogen ions which facilitated diffusion of the surface atoms and H atoms which passivated the defects.



## 1. Introduction

Si nanocrystals (Si NCs) in $SiO_2$ matrix are believed to be a promising material for semiconductors, optoelectronics and photovoltaic solar cells [1–3]. Impurity doping will be very important for the enhancement of conductivity and efficiency of light emission such as photoluminescence (PL) and electroluminescence [4–6]. Boron (B) is one of the most commonly used impurities for preparing p-type Si NCs [5–7].

Depositing B-doped silicon-rich $SiO_2$ (SRO) thin films with subsequent high-temperature annealing is one of the most popular methods for preparing $SiO_2$-matrix B-doped Si-NC (BDS) thin films [4–8]. Most of the B-doped Si NCs were "geometrically isolated" in the amorphous matrix [4,7,8]. The dangling bonds and other defects (non-bridging oxygen hole center, dangling bonds and oxygen-related defects) preferentially generated at the grain boundaries, which would reduce the carrier concentration and efficiency of light emission [9–11]. In addition, the boron atoms preferentially substitute three-fold Si atoms due to dangling bonds at the $SiO_2$/Si NCs interfaces. The hydrogen passivation of defects is effective for the enhancement of structural and electrical properties of BDS thin films [10]. Hong et al. [12] pointed out that the boron-doped Si NCs were passivated by heating the Si-NC thin films at 650 °C for 60 min under $H_2$ flow. However, the H atoms can more easily enter in Si NCs and passivate defects compared with $H_2$ molecules, as seen in amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) thin films [13–15]. Fukata et al. [15] found that significant enhancement of PL was attained for Si-NC thin films by using H atoms or $H_2$ molecules. They also found that the hydrogen-atom treatment significantly shorten the passivated time compared with the hydrogen-molecule treatment.

The diffusion energies of both $H_2$ molecules and H atoms are only dependently controlled by the temperature [15,16]. Increasing the temperature could enhancement of PL intensity. But the higher temperature would cleavage the Si—H bond. In addition, the passivated processes were tedious, usually 1–2 h. Hydrogen-ion implantation is an alternative method for the deposition of a-Si:H thin films [17–19]. The energies of H ions/atoms can be controlled by hydrogen-ion power. The energy or momentum of H ions/atoms can be transferred to the surface Si atoms and O atoms through ion bombardment, improving the diffusion of atoms and the thin-film structure. Huang et al. [20] reported that the effect of hydrogen-ion energy on the structure of a-Si:H thin films. Wang et al. [21] reported the boron-doped a-Si:H thin films deposited by ion-source-assisted magnetron sputtering under different argon-ion-source energies. They found that the thin film deposited under optimal ion-source energies could improve the structural order and reduce the defect density of the a-Si:H thin films.

It should be noted that hydrogen-ion-assisted treatment has significant impacts on the properties of thin films. To our knowledge, the effects of hydrogen-ion energy on the electrical and structural properties of BDS thin films are still not well studied. In this work, the

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BDS thin films were modified by using of hydrogen-ion implantation. The effects of hydrogen-ion energy on the structural and electrical properties of BDS thin films were investigated systematically using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and Hall measurements. In addition, this work provided a mean to achieve the low-resistivity BDS thin films.

## 2. Experimental details

A J-sputter8000 magnetron sputtering system, equipped with four magnetron sources was used for B-doped SRO thin films at room temperature. The substrates were quartz glass and double-sided polished silicon wafers used for different measurements. The substrates were cleaned by ultrasonic baths of acetone and distilled water for about 60 min each. The radio frequency (RF) power of heavily B-doped Czochralski silicon targets (4 in.) and $SiO_2$ targets (4 in.) were set as 120 W and 60 W, respectively. The resistivity of heavily B-doped Czochralski silicon was about $1.0 \times 10^{-3}$ Ω·cm, this resistivity corresponded to a B concentration of ~$1.17 \times 10^{20}$ $cm^{-3}$ [6]. The thickness of the as-deposited thin films was ~450 nm, determined by the profilometer (Veeco Dektak150). The composition of the thin films was ~ $SiO_{1.0}$, measured by XPS (Shimazu, AXIS ULTRADLD). After deposition, the B-doped SRO thin films were subjected to rapid thermal annealing (RTA) for Si-NC formation followed by Kaufman-type hydrogen-ion implantation. The RTA was performed in argon (Ar) ambient at 1100 °C for 60 s. The hydrogen-ion energy was varied from 100 to 500 eV, the hydrogen-ion current, substrate temperature and processing time were fixed at 20 mA, 300 °C and 60 min, respectively. The BDS thin films treated without hydrogen-ion implantation was used as reference.

The chemical compositions and interatomic chemical bonds of both as-deposited and hydrogen passivated BDS thin films were analyzed by XPS (photon energy = 1486.6 eV). The XPS measurements were carried out after a 50 s, 100 s, 200 s and 400 s Ar ion sputter etching. The Ar ion bombardment etching rate was approximately 2.0 Å/s. The XPS spectra were calibrated by using the C 1s peak (284.5 eV) as internal standard. The chemical composition was also studied by FT-IR (Thermo, NICOLET 6700) in the spectral range between 400 and 2000 $cm^{-1}$ with a resolution of 1 $cm^{-1}$. The double-sided polished silicon wafers were used as substrates. The structures of the BDS thin films were measured by Transmission Electron Microscopy (TEM, FEI Tecnai F20). The PL (Renishaw, InVia-Reflex) of the BDS thin films was studied at room temperature using a Nd:YAG laser (532 nm). Samples on quartz substrates were used for studies. Conductivity of BDS thin films were measured by a Hall system (Nanometrics, HL5500PC).

## 3. Results and discussion

Fig. 1 shows the FT-IR spectra of BDS thin films modified with hydrogen-ion energy of 0–500 eV. The peaks at about 460, 880, and 1000–1100 $cm^{-1}$ of characteristic of silicon oxide films, are due to the O-Si-O rocking, Si-O-Si bending, and Si-O-Si asymmetrical stretching vibrations [22,23], respectively. It was observed that there was no significantly change among the modified BDS thin films with different hydrogen-ion energy. It is known that the FT-IR signal comes from the thin-film internal information on the chemical bonds and the structural order [6,22]. The results indicated that hydrogen-ion implantation exerted little effects on the internal structure of the BDS thin films.

Fig. 2(a) and (b) show the XPS spectra of the 100 eV (a) and 500 eV (b) - modified BDS thin films with different etching depth. The Si 2p peak was fitted into five chemical states, corresponding to $Si^0$ (99.3 eV), $Si^{1+}$ (100.3 eV), $Si^{2+}$ (101 eV), $Si^{3+}$ (101.9 eV), and $Si^{4+}$ (103.3 eV) [4,22–24]. The O 1s peak was fitted into two chemical states: $O^{2-}$ the one in $Si\text{-}O_4$ clusters (532.6 eV) and $O^{4/x-}$ in $Si\text{-}Si_x\text{-}O_{4-x}$ ($1 < x < 3$) clusters (<532.6 eV), respectively [22,23]. The peaks of

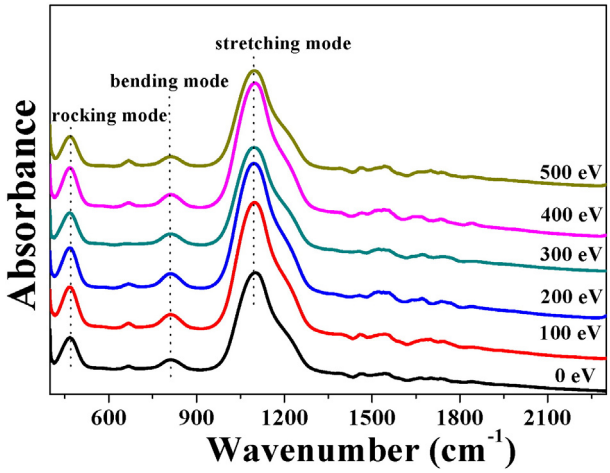


**Fig. 1.** FT-IR spectra of the $SiO_2$-matrix boron-doped Si-NC thin films were modified with hydrogen-ion energy of 0–500 eV.

$Si^{4+}$ and $O^{2-}$ were reduced in intensity with the increase of etching depth, which indicated that more $Si\text{-}Si_x\text{-}O_{4-x}$ ($1 < x < 3$) clusters were separated into $Si\text{-}Si_4$ and $Si\text{-}O_4$ clusters in the surface of modified BDS thin film compared with its interior structure. In addition, it was

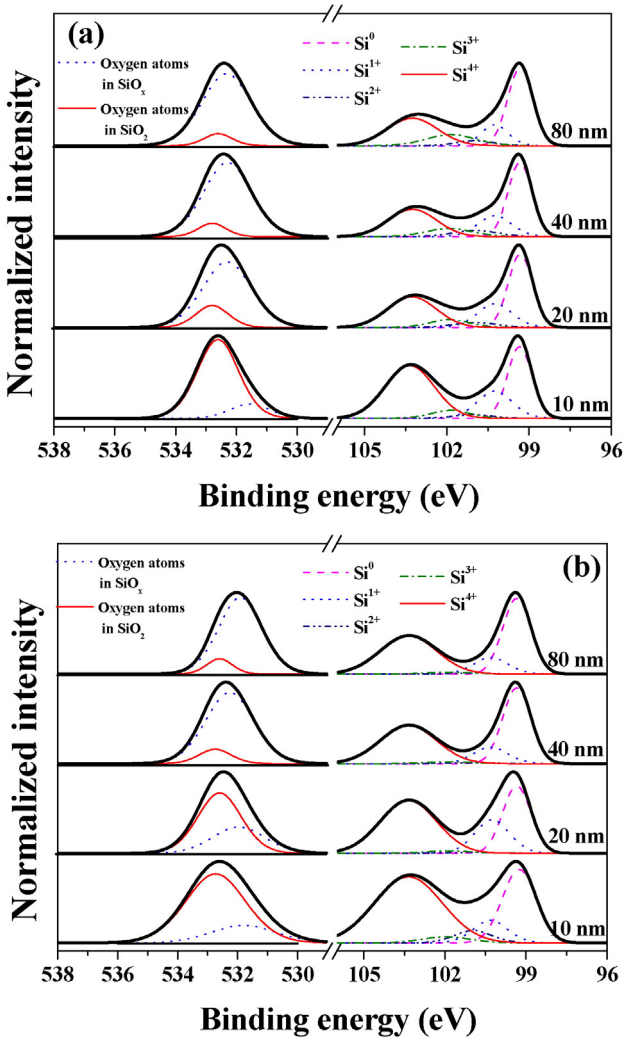


**Fig. 2.** XPS spectra of the 100 eV (a) and 500 eV (b) - modified $SiO_2$-matrix boron-doped Si-NC thin films with different etching depth.