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Synthesis of Boron-Doped Silicon Film Using Hot Wire Chemical Vapor Deposition Technique

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Abstract: Boron-doped polycrystalline silicon film was synthesized using hot wire chemical vapor deposition technique for possible application in photonics devices. To investigate the effect of substrate, we considered Si/SiO_2, $glass/ITO/TiO_2$, Al_2O_3, and nickel tungsten alloy strip for the growth of polycrystalline silicon films. Scanning electron microscopy, optical reflectance, optical transmittance, X-ray diffraction, and I-V measurements were used to characterize the silicon films. The resistivity of the film was 1.3×10^{-2} Ω-cm for the polycrystalline silicon film, which was suitable for using as a window layer in a solar cell. These films have potential uses in making photodiode and photosensing devices.

Keywords: p-type silicon; thin film; HWCVD; photosensor

1. Introduction

Hydrogenated intrinsic polysilicon film can reduce the cost of optoelectronics device significantly. The prospects of intrinsic polysilicon films for thin-film solar cell and other optoelectronic device fabrication using hot wire chemical vapor deposition (HWCVD) were well evaluated [1]. The intrinsic silicon film requires controlled doping to make the films suitable for optoelectronic device application. Boron-doped highly conducting 0.08 $(\Omega cm)^{-1}$ polycrystalline silicon films were optimized using HWCVD for solar cell application [2–4]. Thin-film solar cell fabricated on plastic substrate at 150 °C also showed the prospect of these films as a cost-effective solution [5]. In this article, we described the growth, optimization, and characterization of boron-doped polycrystalline silicon films synthesized using HWCVD. To investigate the effect of nature of substrate on crystallinity of grown boron-doped silicon film, we considered four different substrates, silicon dioxide on silicon wafer (Si/SiO_2), titanium dioxide on glass ($glass/ITO/TiO_2$), sapphire (Al_2O_3), and nickel–5%tungsten alloy textured metal strip (Ni-W) with dominant (002) orientation. Basic motivation for carrying out growth on different types of substrates came from the works of Green et al. [6], Teplin et al. [7], and Findikoglu et al. [8], who showed growth of textured silicon films on amorphous substrates. SiO_2 on Si is an amorphous substrate. Sapphire is chosen as a robust substrate and Ni-W is chosen as a flexible substrate. A range of experiments were conducted by varying the growth conditions to optimize the crystalline quality of silicon film with an intention to use the film in a solar cell [9,10]. Thin-film solar cells of p-i-n structure have i-layer as the light absorber and p-type layer as a window. At the initial stage, we conducted experiments for the synthesis of p-type polycrystalline silicon layers on a variety of substrates.

2. Experimental Section

2.1. HWCVD System Used for Synthesis and Other Apparatus

The HWCVD system used in this work [11] was custom made of stainless steel with provision of a window for monitoring the tungsten filament temperature. Single filament of tungsten wire, 65 cm long and 0.5 mm in diameter, wound in a zigzag shape was resistively heated to 1900 °C using a DC power supply. The filament was placed at about 5 cm height above the substrate. The area covered by the filament was about 9 cm × 9 cm. The hot filament radiatively heated the substrate to 200 °C as measured with a thermocouple in contact with the substrate surface in a temperature calibration run. Higher substrate temperature was achieved by a resistive heater placed in contact with the substrate holder from below. A moveable shutter between the wire and the substrate allowed several growth steps to be performed with definite starting and ending point for each step during the growth of the film. The gas flow shower was located above the filament. The vacuum system had base pressure of 1×10^{-6} mbar, and it was equipped with a load lock to avoid exposing the system to room ambient while loading and unloading the samples. A mixture of pure SiH_4 and pure H_2 was used as a process gas for the intrinsic silicon film. Diborane (5% diborane and 95% hydrogen) gas was introduced as a source of boron for p-type silicon film. For film thickness measurement, a DektakXT stylus profiler, from Bruker, Billerica, MA, USA, was used.

Si/SiO$_2$ substrates were prepared by oxidizing 500 nm of silicon dioxide on 2-inch (100) silicon wafers using a wet oxidation process. We used one-fourth of the 2-inch diameter silicon wafer for the growth process. Sapphire (Al_2O_3) substrates were 1 cm × 2 cm and were cut from 0.5 mm thick, c-axis oriented, both sides polished, two inch diameter wafer, and were obtained from Semiconductor Wafer Inc. Titanium dioxide (TiO_2) substrates (1 cm × 2 cm) were (112) oriented anatase, prepared by atmospheric chemical vapor deposition (ACVD) techniques, on indium tin oxide (ITO)-coated glass, and were synthesized at the Washington University [12]. The interest in this substrate was not for optoelectronics, but for its application as electrode for energy storage. We used nickel–5% tungsten (Ni-W) metal tape (1 cm × 2 cm) [13] of about 80-micron thickness, biaxially textured Ni-W substrates with dominant (002) orientation, obtained from EVICO GmbH, as metal substrate.

2.2. Growth of Boron-Doped Polycrystalline Silicon Film

The growth began with a nucleation step at 400 °C. This was based on the experiments of Vallat-Sauvain et al. [14] who showed that the silicon grains synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD), using a dilute mixture of silane with hydrogen, developed preferential (220) orientation for a certain ratio of SiH_4/H_2 precursors. In our experiments, we used H_2:SiH_4 in the ratio of 20:1 for duration of 100 s.

Boron-doped silicon films were grown on various substrates using HWCVD, starting with a thin silicon nucleation layer at 400 °C substrate temperature. The substrate temperature was ramped from 400 °C to 600 °C for higher surface mobility of silicon atoms to continue the growth. Table 1 shows the growth conditions for the thin and thick film, respectively.

The growth of boron-doped polysilicon layer was done by two schemes. In the first scheme, the gas mixture remained the same as used for the nucleation stage. In the second scheme, the growth of silicon layer proceeded in five stages after the nucleation stage, with gradual increasing concentration of SiH_4 as listed in Table 1. The silane flow rate was increased in steps while simultaneously decreasing the H_2 flow rate in order to keep the chamber pressure constant. To facilitate the measurement of thickness, we placed a piece of silicon, covering one end of the Si/SiO$_2$ substrate, as mask. This allowed us to measure the step height using surface profiler. The thickness, as shown in the Table 1, is for the boron-doped silicon film on Si/SiO$_2$ substrate.

Table 1. Growth parameter of boron-doped p-type polycrystalline silicon films on Si/SiO$_2$, sapphire (Al$_2$O$_3$), glass/ITO/TiO$_2$, and Ni-W substrates.

Exp. No.	Sample Name	Process Pressure in mbar	Substrate Temp. in °C	Gas Flow in Sccm H$_2$:SiH$_4$:5%B$_2$H$_6$	Growth Duration in Sec	Film Thickness in nm
		Two-stage growth (thin film)				
1	18_Si/SiO$_2$ 24_Al$_2$O$_3$ 25_Glass/ITO/TiO$_2$	2.4 × 10^{-1}	400	15:1:5	110	218
		2.5 × 10^{-1}	600	15:1:5	1000	
	26_Ni-W	Six-stage growth (thick film)				
		2.3 × 10^{-1}	400	15:1:5	100	
	2_Si/SiO$_2$ 27_Glass/ITO/TiO$_2$ 29_Ni-W 30_ Al$_2$O$_3$	2.1 × 10^{-1} to 2.3 × 10^{-1}	600	15:1:5	100	1085
2				15:1.5:5	100	
				13:2:5	100	
				12:3:5	100	
				10:5:5	1000	

3. Results and Discussion

3.1. SEM Image Analysis

We took scanning electron microscope (Zeiss Ultra 55 SEM with Oxford EDX) images to observe the grain size and shape in p-type polycrystalline silicon films.

Figure 1 shows morphology of silicon thin films grown on different substrates following the recipe given in Table 1, Experiment Number 1. Films on Si/SiO$_2$ and Al$_2$O$_3$ substrate had similar shaped circular grains with average grain size of 30 nm. Grains on glass/ITO/TiO$_2$ substrate were not circular in shape and average grain size was larger, about 100 nm. The shape of crystalline grains on nickel substrate was rather different from the shapes observed in all other substrates. Grains were randomly oriented, merged together to form larger grains of 400 nm, and in some portion, a columnar growth was also observed.

Figure 2 shows morphology of thick polycrystalline silicon film grown on different substrates following the recipe given in Table 1, Experiment Number 2. Films grown on Si/SiO$_2$, glass/ITO/TiO$_2$ and Al$_2$O$_3$ substrates had grain size of 100 nm, and the shapes were similar to those observed in the case of intrinsic silicon film [15]. Grains on nickel substrate looked different. Grains were merged and two to three microns in size. Sharp, pointed four-micron features were observed due to the contribution from the Ni-W substrate effect. We looked at the TEM of undoped silicon films grown on Si/SiO$_2$ substrate using the same gas mixture, except for diborane, and same growth procedure [16]. The nucleation layer was about 10 nm thick. The layer immediately above the nucleation layer, about 0.2 micron thick, was of very high crystalline quality as seen from selective area diffraction (spotty pattern). The top layer, however, had more polycrystalline nature (rings diffraction pattern). This aspect requires further investigation.
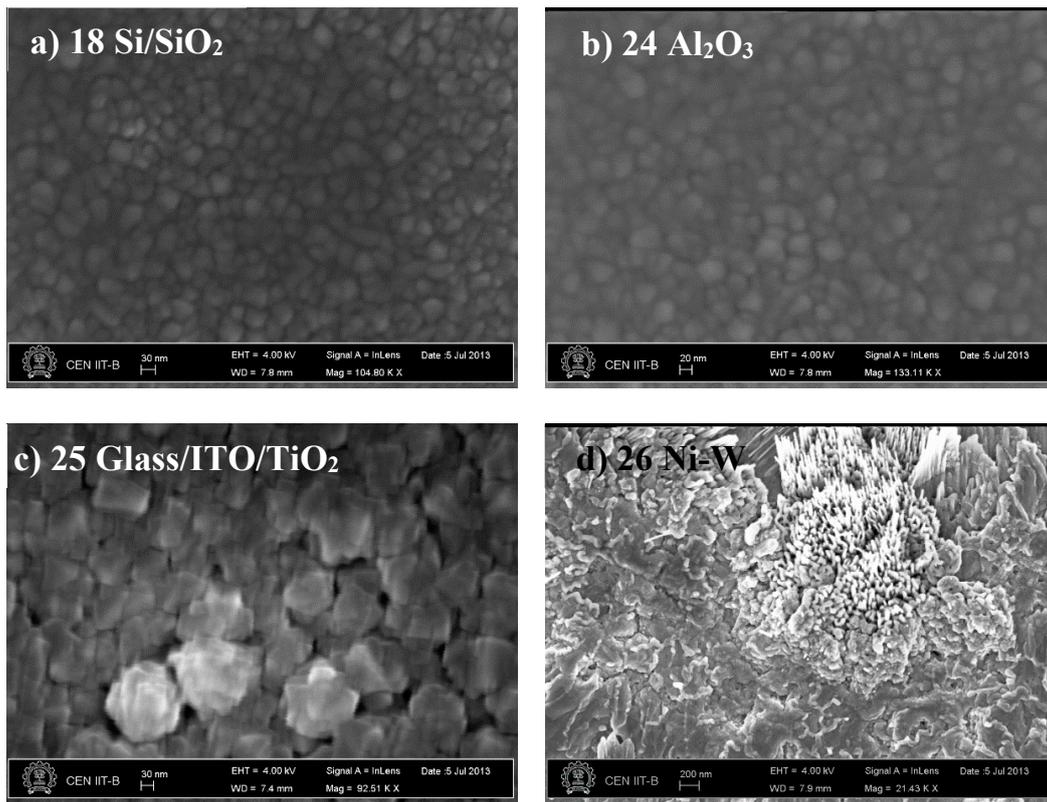
Figure 1. SEM image of boron-doped p-type polycrystalline silicon thin film (Exp. 1) on (**a**) Si/SiO$_2$, (**b**) Al$_2$O$_3$, (**c**) glass/ITO/TiO$_2$, and (**d**) Ni-W.
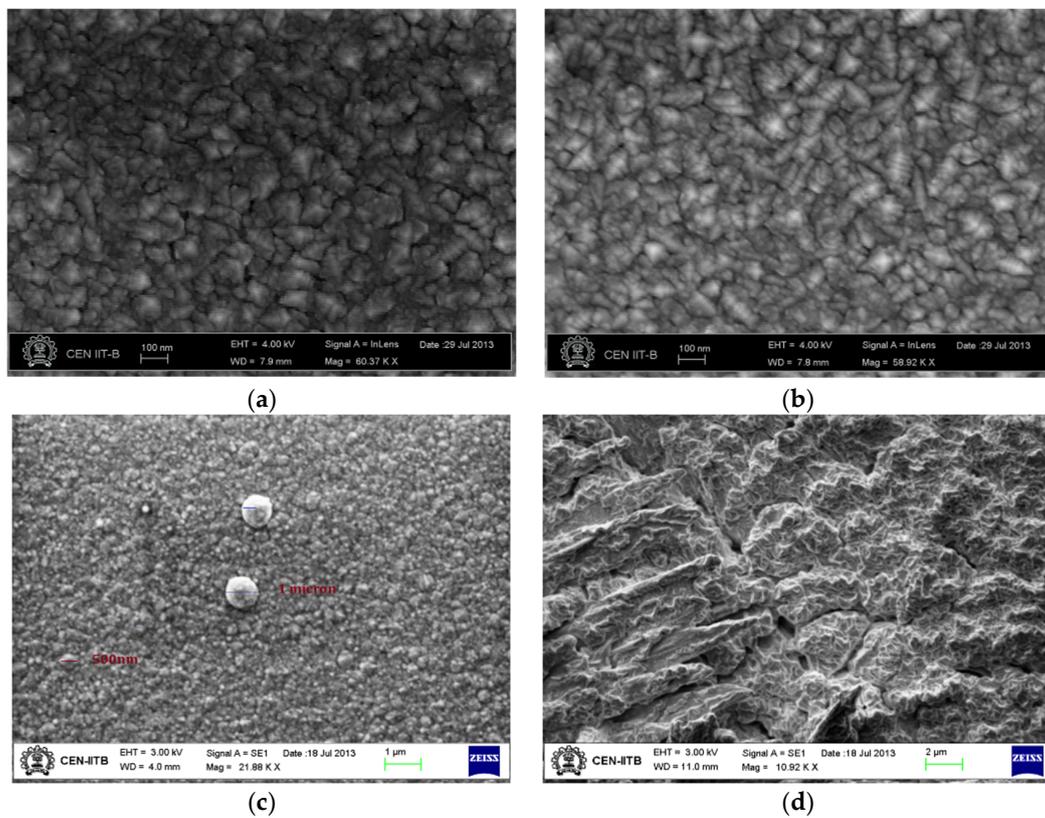
Figure 2. SEM image of boron-doped p-type polycrystalline silicon thick film (Exp. 2) on (**a**) Si/SiO$_2$, (**b**) Al$_2$O$_3$, (**c**) glass/ITO/TiO$_2$, and (**d**) Ni-W substrates.

3.2. Crystal Orientation

Structural characterization of silicon films was performed using CuK_α radiation from high-resolution X-ray diffraction (XRD) instrument, SmartLab 3 kW, from Rigaku Corporation, Japan, operated at 40 keV, 40 mA, and CuK_α in θ–2θ geometry. XRD measurements for thick boron-doped polycrystalline silicon film grown on Si/SiO_2, glass/ITO/TiO_2, Al_2O_3, and Ni-W substrates are shown in Figure 3. All the data were taken at 2θ in the range of 20°–60°. XRD patterns contained peaks corresponding to the silicon film as well as the substrates. Broad hump in XRD of the Si/SiO_2 substrate at 2θ less than 36° was due to the scattering from amorphous SiO_2. Some of the substrate peaks were marked in Figure 3. Strong peaks corresponding to the sapphire and (002) textured Ni-W substrates appeared at 2θ equal to 42° and 51°, respectively, which were removed to facilitate the presentation. For analysis purpose, we considered the three peaks at 2θ values of 28.5°, 47.5°, and 56° for the boron-doped polycrystalline silicon planes (111), (220), and (311), respectively. The peaks corresponding to (220) increased significantly for silicon film on Si/SiO_2, glass/ITO/TiO_2, and Al_2O_3 substrates. Hence for thick boron-doped polycrystalline silicon film (220), a preferred growth direction was observed. Boron-doped polycrystalline silicon film on Ni-W substrate showed no preferred crystal orientation. This result was different from the result of Teplin et al. [7], who obtained nearly epitaxial films using several intermediate oxide layers. It was possible that silicon reacted with nickel, and prevented growth of silicon nuclei in the initial stages so that the growth turned out to be random.
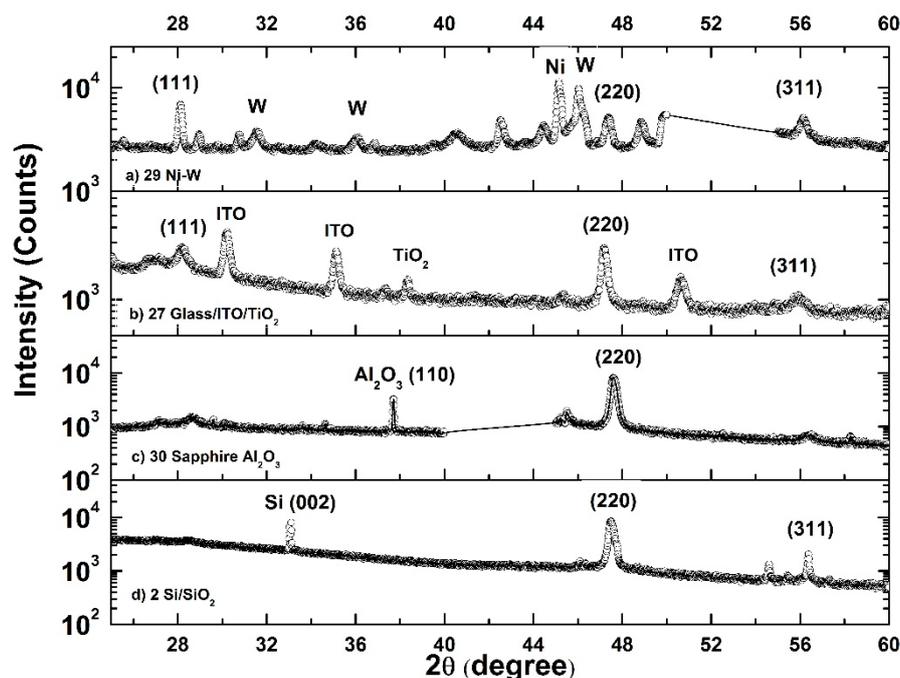

Figure 3. Diffraction spectrum of thick boron-doped polycrystalline silicon film on (**a**) 29_Ni-W-pSi, (**b**) 27_ Glass/ITO/TiO_2-pSi, (**c**) 30_Sapphire-pSi (Al_2O_3), and (**d**) 2_Si/SiO_2-pSi substrate.

3.3. Optical Transmission and Reflectance

Transmission and reflectance spectra allowed us to evaluate the optical properties of boron-doped silicon films in the Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) range of wavelengths. We took transmittance and reflectance spectra for the silicon film on sapphire (Al_2O_3) substrates using PVE300 spectrometer from Bentham Inst. Ltd., and these are shown in Figure 4. Interference oscillations were observed at wavelengths longer than 500 nm for silicon film on sapphire substrates as the film on this substrate was smooth. No transmission measurement was performed for the silicon films deposited on Si/SiO_2 and nickel substrates, since these substrates absorb light of wavelengths in the range of interest.

Reflectance spectrum measured on Si/SiO$_2$ substrate was similar to that measured on the sapphire substrate. The overall reflection was 30% or lower.
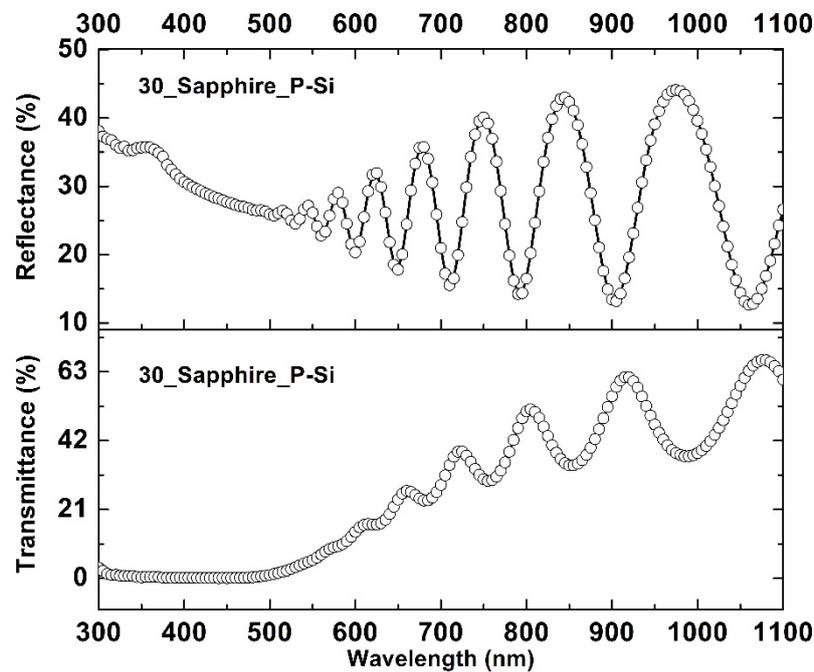

Figure 4. Reflectance spectrum of boron-doped p-type polycrystalline silicon film on sapphire (Al$_2$O$_3$) substrates. Transmission spectrum of boron-doped p-type polycrystalline silicon film on sapphire (Al$_2$O$_3$) substrates.

These experiments showed that optical quality of film is suitable for use in a p-i-n solar cell with the thickness modified as required by the device design.

3.4. Resistivity Analysis

Sheet resistivity and bulk resistivity of the films were measured using collinear four-point probe apparatus by Lucas-Signatone Corp. The measurements for boron-doped silicon film grown on Si/SiO$_2$ and on sapphire substrates are shown in Table 2. In comparison, the resistivity of undoped films was about 2–4 × 10^5 ohm-cm (these measurements were done with deposited contacts using electrometer) [15]. Doping with boron lowered the resistivity by several orders of magnitude as expected. Relatively higher resistivity was observed for thick polycrystalline silicon film on 2_Si/SiO$_2$ and 30_Al$_2$O$_3$ substrate compared to the thin silicon film. This may be due to the change in the gas composition for thicker growth, with larger silane content and corresponding reduction in the diborane to silane ratio. As given in Section 3.1, the TEM results showed better crystallinity for the layer adjacent to the nucleation layer. This may be also contributed to the differences in the resistivity. From the EDX measurement, the presence of oxygen was noticed though we took it as contamination. No I-V measurements were done on p-type silicon film on nickel and glass/ITO/TiO$_2$ substrates using four-probe setup because these substrates had back conducting metal.

Table 2. Resistivity of boron-doped silicon film on Si/SiO$_2$ and Al$_2$O$_3$ substrates.

Sample Name	Voltage Volt (V)	Current Amp (I)	Sheet Resistance = (V × 4.532)/I ohm/square	Thickness cm	Resistivity Ohm-cm
Polycrystalline silicon thin film					
18_Si/SiO$_2$	1.35	1×10^{-2}	6.12×10^2	2.18×10^{-5}	1.33×10^{-2}
24_Al$_2$O$_3$	1.67	1×10^{-2}	7.6×10^2	2.18×10^{-5}	1.65×10^{-2}
Polycrystalline silicon thick film					
2_Si/SiO$_2$	0.93	1×10^{-2}	4.2×10^2	1.1×10^{-4}	4.64×10^{-2}
30_Al$_2$O$_3$	1.58	1×10^{-2}	7.2×10^2	1.1×10^{-4}	7.88×10^{-2}

4. Conclusions

Our experiments showed that one-micron thick p-type boron-doped silicon films prepared at 600 °C are preferentially oriented along (220) direction. We achieved fairly high average growth rates (about 7 A°/s) for the thick films by increasing the silane content in the gas mixture. However, the average grain size remained small on Si/SiO$_2$ and Al$_2$O$_3$ substrates. The resistivity of the thin films was in the range of 1.3–1.7×10^{-2} Ω-cm, while in the thicker films, the resistivity was in the range of 4.64–7.88×10^{-2} Ω-cm. This increase in resistivity was may be due to the reduction in the ratio of diborane to silane by a factor of 5 in the thicker films compared to that in the thinner films. By optimizing the thickness and doping concentration, these films can have potential application in optoelectronics devices.

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