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P-Doped Polycrystalline Silicon Films Obtained At Low Temperature By Hot-Wire Chemical Vapor Deposition

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Abstract

P-doped polycrystalline silicon films were deposited over Corning 7059 substrates at moderate temperature, 330 °C, in a hot wire reactor. The films were obtained from the decomposition of silane and hydrogen (10 % SiH_4, 90 % H_2) and different amounts of diborane. The structure and morphology of samples were studied with X-ray diffraction (XRD), Raman-spectroscopy and Scaning Electron Microscopy (SEM). X-ray diffraction spectra show sharp diffraction peaks corresponding to silicon reflections, and Raman spectra show no evidence of amorphous phases and present a high intensity and narrow peak at 520 cm^{-1}, which is the typical feature of crystalline silicon structure. The efficiency of boron incorporation was studied by Secondary Ion Mass Spectrometry (SIMS). The electrical properties of doped samples were also studied.

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Introduction

There is an interest in polycrystalline silicon (poly-Si) films due to their wide range of optoelectronic applications in large-area semiconductor devices, such as thin film transistors (TFT), and also in photovoltaic applications.

Poly-Si films are obtained by various methods, such as low-pressure chemical vapor deposition (LPCVD)[1], crystallization by rapid thermal process (RTP)[2] and solid phase crystallization (SPC)[3]. In these techniques poly-Si is obtained at temperatures around 600 °C.

In this study we use the hot-wire chemical vapor deposition (HWCVD) to obtain poly-Si fims at moderate temperatures. HWCVD technology has been used to obtain hydrogenated amorphous silicon (a-Si:H) of good quality for photovoltaic applications [4]. In this process the heated filament induces silane pyrolytic dissociations and produces, in addition to silyl radicals, atomic hydrogen, which reacts with silane molecules to produce SiH_3 radicals.

In a previous paper [5] we have shown the possibility of using the HWCVD technique to obtain thick undoped poly-Si films at fast growth rates and moderate temperatures, thus allowing the use of standard glass substrates. In this paper we have studied the feasibility of growing poly-Si films doped with boron by HWCVD. A set of five samples, one undoped and others obtained from different diborane doping levels, was studied with Scanning Electron Microscopy (SEM), X-ray Diffraction (XDR), Raman Spectroscopy and Secondary Ion Mass Spectrometry (SIMS).

Experimental

The films were deposited on glass substrates (Corning 7059) in a hot-wire reactor. The main deposition parameters are listed in Table 1. The reaction gases were activated by a folded tungsten filament 1 mm thick and 150 mm long. The filament covered the whole sample surface homogeneously. The filament temperature was set to 1600 °C as measured by an optical pyrometer. The substrate temperature was measured by a calibrated thermocouple attached to the substrate holder.

The samples were deposited from a mixture of 10 % silane and 90 % hydrogen (2 sccm SiH_4 and 18 sccm H_2) and variable amounts of diborane (B_2H_6) diluted 1% in H_2, ranging from $4.7x10^{-2}$ to 1.03 sccm, were added to the deposition gases. The substrate

temperature was maintained at 330 °C, which corresponds to a filament-substrate distance of 3 cm. The total gas pressure was 21 Pa.

All films were morphologically and structurally characterized by SEM, Raman Spectroscopy and XRD. Dark conductivity and its activation energy was established from standard electrical measurements. These were performed in vacuum using evaporated coplanar Cr electrodes, 1 cm in length and 1 mm apart.

Results and discussion

The study of the obtained films shows the possibility of growing large columnar crystalline structures at moderate temperatures and high deposition rates. The crystalline structure of these doped samples was obtained by Raman and XRD analysis. Figure 1 shows the Raman spectra of samples obtained from different diborane/silane ratios in the gas phase. The spectra present a narrow, high intensity peak centered around 517 cm^{-1}. The shift of the peak with respect to the position of monocrystalline silicon Raman peak (522 cm^{-1}), its linewidth and its asymmetry are characteristic of poly-Si scattering [6]. Boron incorporation has little influence on the crystallinity of the films. When increasing diborane/silane ratio, a slight shift of Raman peaks toward lower wavenumber and an increase in their linewiths are observed. The peak position shifts from 517 cm^{-1} for the undoped sample to 515 cm^{-1} for the sample obtained at the highest concentration of diborane, whereas, the full width at medium high (FWMH) varies from 8 cm^{-1} to 13 cm^{-1}. These effects are related to a decrease in crystal sizes [6]. In spite of the boron effect in the Raman crystalline peak, the band attibuted to amorphous silicon, centered around 480 cm^{-1}, is not observed, so we deduce a dominant silicon crystalline phase in all the samples.

In Figure 2, X-ray diffraction spectra of samples obtained from different boron concentration are shown. X-ray spectra show the main silicon diffraction peaks, indicating the crystalline structure of all the films, in the range of diborane concentration studied.

The morphology and structure of polycrystalline samples were studied by SEM analysis. Figure 3a shows the cross-sectional view of the sample obtained at the highest concentration of diborane. The cross-sectional view shows a columnar structure, which is a general feature of all the samples. The growth rate, calculated from thicknesses obtained from cross-sectional SEM images, was of the order of 25 Å/s for all the samples, and no

was found between growth rate and diborane concentration. Figure 3b shows the surface image of the same sample, revealing a granular structure with grain sizes ranging from 0.3 μm to 0.8 μm. Surface morphology and grain sizes were not affected by boron incorporation.

The study of boron incorporation was performed by SIMS analysis. SIMS depth profiles of silicon and boron show a constant level in the bulk of the film. In all the samples the silicon signal was very similar, which allows us to refer the boron content to the silicon content and compare the different doped samples. In Figure 4, the ratio between B and Si signals is represented as a function of diborane/silane ratio in gas phase. Results show that boron is incorporated into the films and its level increases almost linearly with the diborane/silane ratio. In the figure, we also plot the solid phase boron concentration as a function of the diborane/silane ratio. The solid phase boron concentration was estimated by comparing these results with a crystalline silicon wafer implanted with boron.

The electrical characteristics of the films doped by diborane were examined by dark conductivity (σ_d) and its activation energy (E_{act}). Figure 5 shows the Arrhenius plot of the conductivity versus 1000/T. An increase in σ_d and a decrease in E_{act} were observed when boron incorporation increased. The activation energy of conductivity, calculated in the exponential region, is 1.28 eV for the undoped sample and decrease to 0.21 eV for a sample doped with a boron atoms to silicon atoms ratio of 1.0×10^{-2}.

A more detailed study is necessary to describe the conduction mechanisms in the samples. In particular, tranversal conductivity measurements are needed to determine the possible existence of anisotropic transport, which is suggested by the columnar structure of these samples. It will also be necessary to determine the mobility and electron concentration to obtain further information about the influence of the grain boundaries in electrical properties.

Conclusions

P-doped polycrystalline silicon films have been obtained by HWCVD from hydrogen diluted silane/diborane mixtures at substrate temperatures as low as 330 °C. Poly-Si films were obtained on amorphous substrates.

Morphological and structural studies performed with XRD, Raman-spectroscopy and SEM show that the structure of p-doped polycrystalline silicon films is little influenced by boron incorporation.

boron incorporation.

The crystalline structure of the poly-Si films have a columnar structure, with crystals extending from the substrates to the top of the films.

In the present experimental conditions the growth rate is very high, being in the order of 25 Å/s, and is not influenced by boron concentration.

The boron content in the films is proportional to the boron concentration in the gas phase.

The present study has demonstrated that HWCVD technique is a promising technique to obtain doped polycrystalline silicon films at low substrate temperature. Moreover, it is expected to be easily scaled up for applications to large area optoelectronic devices and to photovoltaic solar cells.

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Table 1. Experimental parameters

Sample	$N(B_2H_6)/N(SiH_4)$	Growth rate (Å/s)	Thickness (μm)
HWD2	$4.7x10^{-4}$	25	4.6
HWD3	$1.0x10^{-3}$	22	3.9
HWD4	$4.1x10^{-3}$	28	4.9
HWD5	$1.0x10^{-2}$	26	4.7
HWD6	0	25	4.6

Figure captions.

Fig. 1. Raman spectra of samples deposited at 330 °C, 2 sccm SiH_4 and 18 sccm H_2 and different amounts of diborane: a) HWD6 $N(B_2H_6)/N(SiH_4)=0$, b) HWD3 $N(B_2H_6)/N(SiH_4)=1.0x10^{-3}$, c) HWD5 $N(B_2H_6)/N(SiH_4)=1.0x10^{-2}$.

Fig.2. XRD spectra of poly-Si samples deposited at 330 °C, 2 sccm SiH_4 and 18 sccm H_2 and different amounts of diborane. Lower plot: HWD2 $N(B_2H_6)/N(SiH_4)=4.7x10^{-4}$. Medium plot: HWD3 $N(B_2H_6)/N(SiH_4)=1.0x10^{-3}$. Upper plot: HWD5 $N(B_2H_6)/N(SiH_4)=1.0x10^{-2}$.

Fig. 3. SEM micrographs of cross-section (a) and surface (b) of sample HWD5 deposited at 330 °C, 2 sccm SiH_4 and 18 sccm H_2 and $N(B_2H_6)/N(SiH_4)=1.0x10^{-2}$.

Fig. 4. Relative boron content for samples as a function of diborane/silane ratio.

Fig. 5. Dependence of conductivity vs 1000/T for samples obtained at different diborane concentration. HWD4 $N(B_2H_6)/N(SiH_4)=4.1x10^{-3}$, HWD5 $N(B_2H_6)/N(SiH_4)=1.0x10^{-2}$ and HWD6 $N(B_2H_6)/N(SiH_4)=0$.

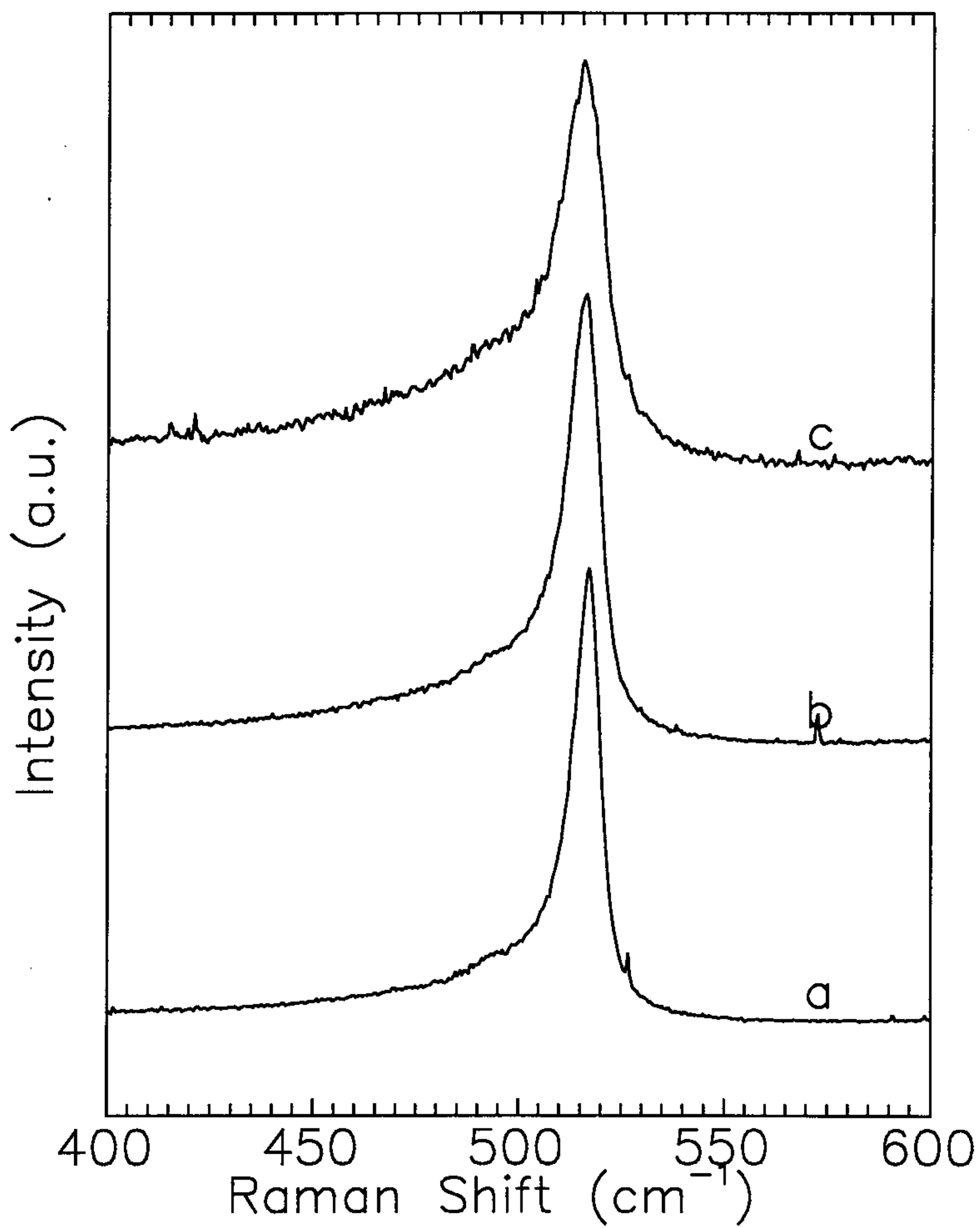

Figure 1

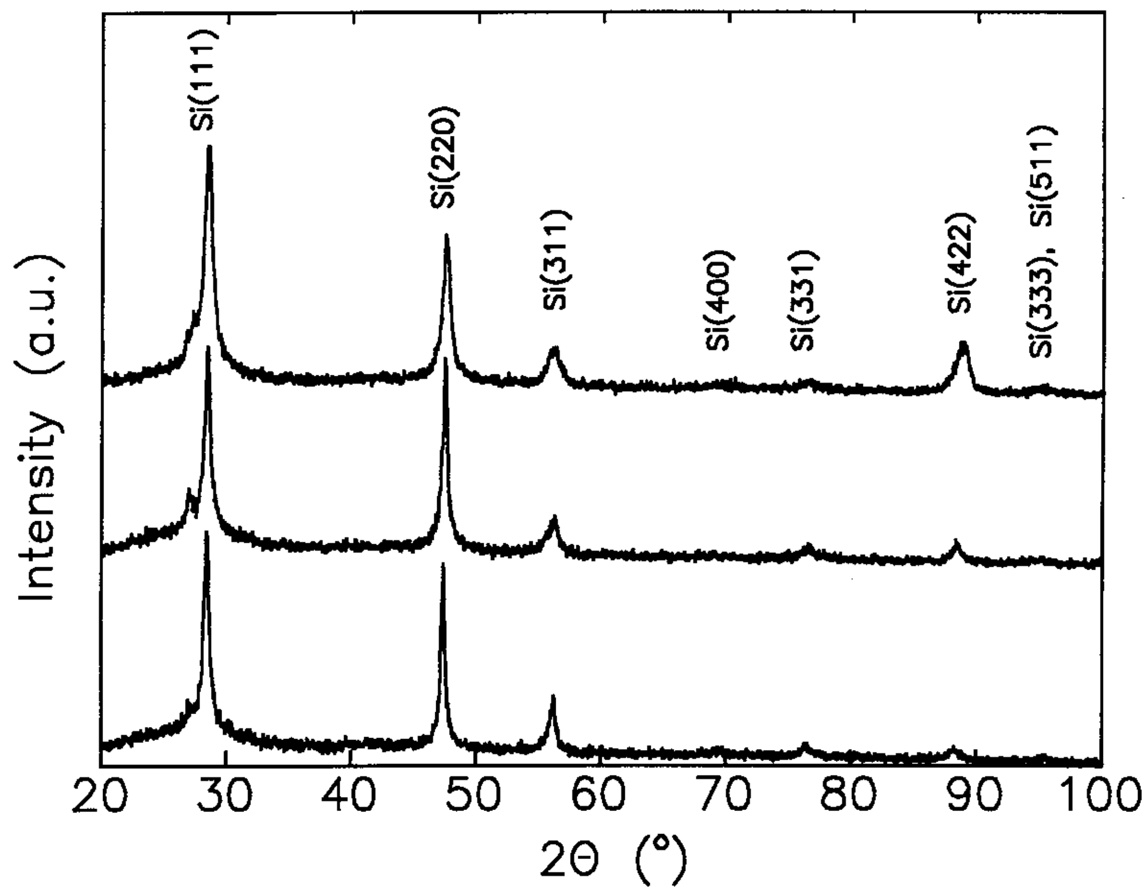

Figure 2

x6.0k 2736 15kV 5um

Fig 3a

Fig 3b

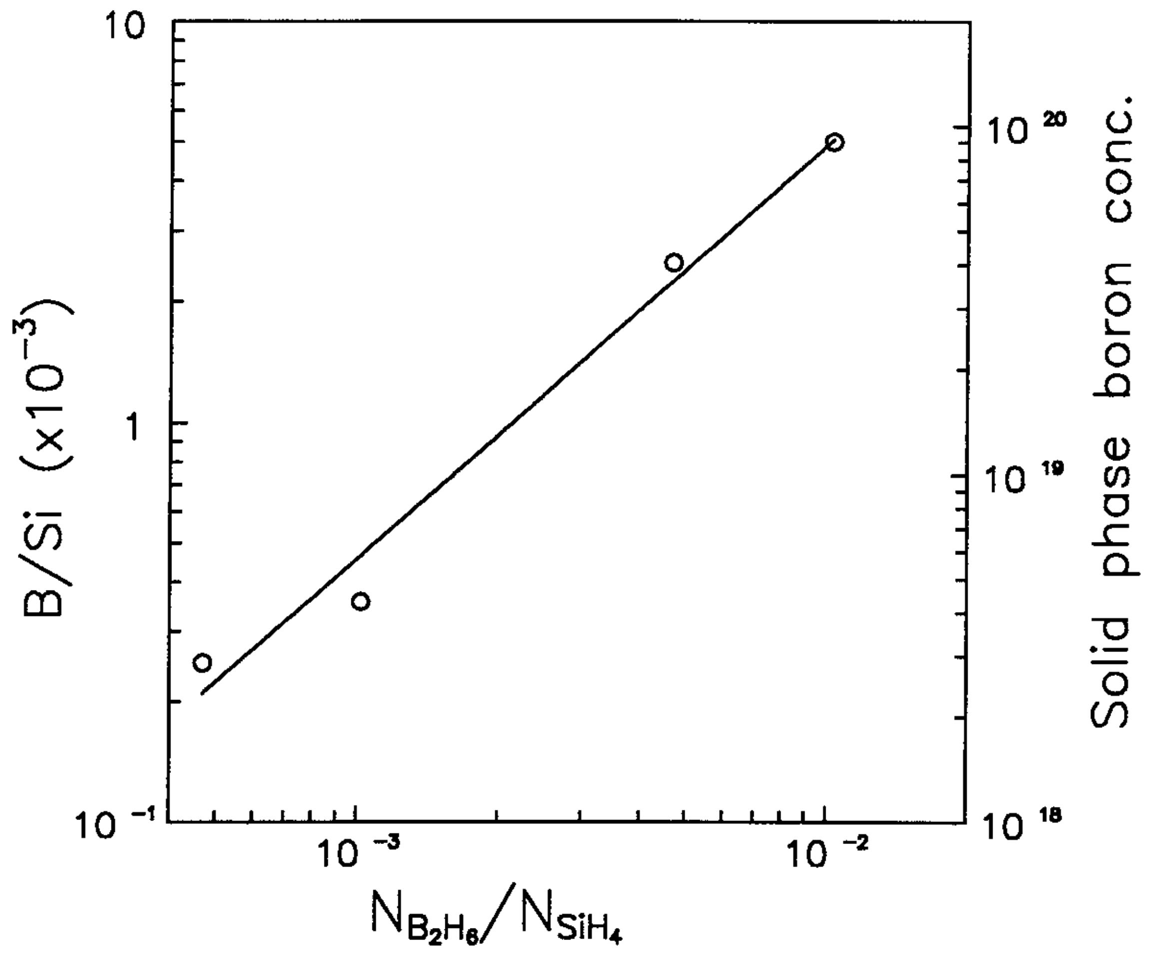

Figure 4

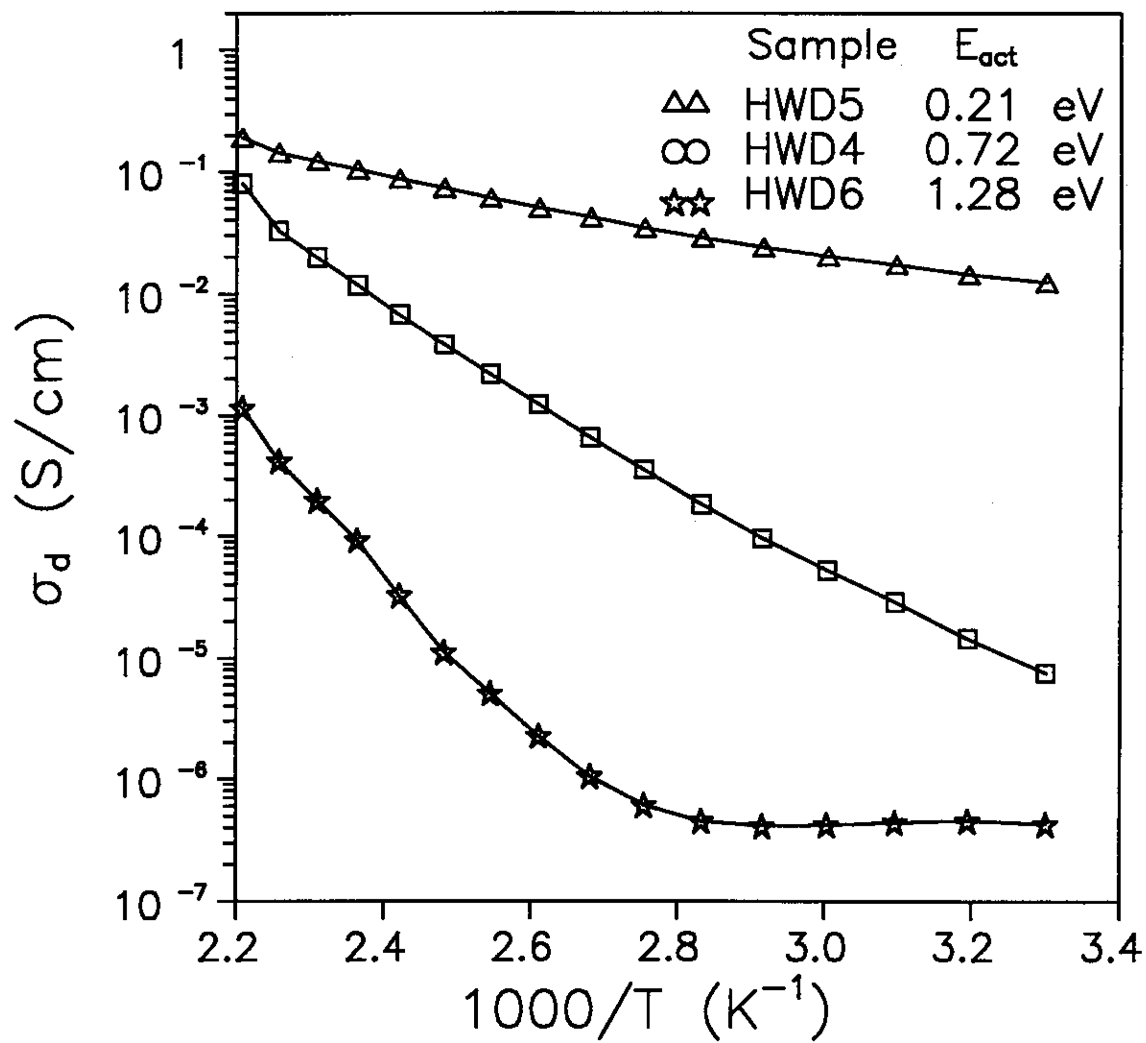

Figure 5