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Comparison of Doping of $Ge_y Si_{1-y}$:H (y>0.95) Films Deposited by Low Frequency PECVD at High (300°C) and Low (160°C) Temperatures

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ABSTRACT

In this work we present the results of comparative study n- and p-doping of Ge:H and $Ge_{0.96}Si_{0.04}$:H films deposited by LF PECVD at high deposition temperature (HT) T_d=300°C and low deposition temperature (LT) T_d=160°C. The concentration of boron and phosphorus in solid phase was measured by means of SIMS technique. Such parameters as spectral dependence of absorption coefficient, room temperature conductivity σ_{RT} and activation energy E_a for both intrinsic and doped films were obtained. The doping range studied in gas phase was for boron $[B]_{gas}$= 0 to 0.15% and for phosphorus $[P]_{gas}$= 0 to 0.2%. In general effect of deposition temperature on P and B doping has been demonstrated. For LT films changes of $[P]_{gas}$=0.04% to 0.22% resulted in more than 2 orders increasing conductivity and reducing activation energy from E_a=0.28 to 0.16 eV. HT films in the range of $[P]_{gas}$=0.04% to 0.2% demonstrated saturation of conductivity. HT films showed continuous reducing E_a with increase of $[P]_{gas}$. In the case of boron doping both HT and LT films had a minimum of conductivity at certain values of $[B]_{gas}$=0.05% (LT films) and 0.04% (HT films) and related maximums of activation energy $E_{a(max)}$ at the same doping with $E_{a(max)}$=0.47 eV for HT and $E_{a(max)}$=0.53 eV for LT films. It suggests a compensation of electron conductivity in un-doped films for low B doping. Further raising $[B]_{gas}$ leads to reducing E_a and the smallest E_a=0.27 eV was obtained at $[B]_{gas}$=0.18% for HT films and E_a=0.33 eV at $[B]_{gas}$=0.14% for LH films.

INTRODUCTION

Germanium-Silicon films deposited by low temperature process (T_d< 250°C) are of much interest because they provide narrow gap materials compatible with plasma deposited Si:H films and the potential applications for the devices on plastic substrates. These films can be used for different device applications i.e., solar cells [1]. Previously the films with low density of localized states obtained by low frequency (LF) PECVD at deposition temperature T_d= 300°C has been reported [2] and doping of these films has been discussed [3]. To our knowledge fabrication and characterization of Ge_ySi_{1-y}:H films with high Ge concentration (y>0.5) obtained by low temperature plasma deposition and n-type and p-type doped films is poorly reported in literature [4-6]. In this work we present a comparison of Ge:H films deposited by LF PECVD at high deposition temperature (HT) T_d=300°C and $Ge_{0.96}Si_{0.04}$:H films deposited at low deposition temperature (LT) T_d=160°C.

EXPERIMENT

The films were grown in capacitive low-frequency (f=110 KHz) discharge with power W=300 Watt and pressure P=0.76 Torr from SiH_4 and GeH_4, PH_3 and B_2H_6 feed gases diluted with H_2 as R= Q_{H4}/(Q_{SiH4}+Q_{GeH4}) with R=75 for LT films (T_d=160 °C) and R=50 (Q_{SiH4} = 0 sccm) for HT films (T_d=300°C) . Boron and phosphorus concentration in gas phase was calculated in the deposition process as $[B]_{gas}$=B_2H_6/2(GeH_4+SiH_4) and $[P]_{gas}$=PH_3/(GeH_4+SiH_4). The range studied for boron doping was from $[B]_{gas}$= 0 to 0.15% for both HT and LT films to compare the compensation effect at low doped concentration in two different films (Ge and SiGe) and the phosphorus doping was studied in the ranges from $[P]_{gas}$= 0 to 0.22 % for $Ge_{0.96}Si_{0.04}$:H films at LT and Ge:H film at HT. The composition, incorporation of boron and phosphorus in gas phase to solid phase was extracted from SIMS measurements.

The absorption coefficient spectra was obtained from spectral transmission measurements and data processing with software PUMA [4]. Conductivity measurements were carried out with Keitley 62517 electrometer in vacuum thermostat (Yanis Inc.). The activation energy E_a was extracted from the measurements of temperature dependence of conductivity.

DISCUSSION

Figure 1 shows for comparison the spectral dependence of the optical absorption coefficient *α(hν)* for intrinsic HT Ge:H and intrinsic HT and LT $Ge_{0.96}Si_{0.04}$:H films. For details about band tail and defect absorption for the selected films, see [2].

The figure 2 shows boron incorporation from gas phase to solid phase. The incorporation of boron in LT $Ge_{0.96}Si_{0.04}$:H films was described by linear fit as $[B]_{sol}$= k_{LTB} $[B]_{gas}$ (k_{LTB}= 4.8 ± 0.7) and the incorporation of boron in HT Ge films was described as $[B]_{sol}$= k_{HTB} $[B]_{gas}$ (k_{HTB}= 4.3 ± 0.2). It is interesting to note that the incorporation of boron is similar for HT Ge:H and LT $Ge_{0.96}Si_{0.04}$:H films.

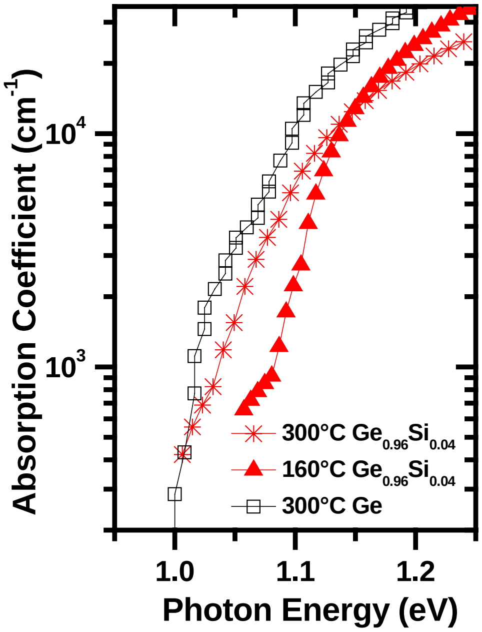


Figure 1. Absorption coefficient spectra α(hv) for intrinsic films (reference films for doping) with different silicon and germanium content at different deposition temperature T_d.

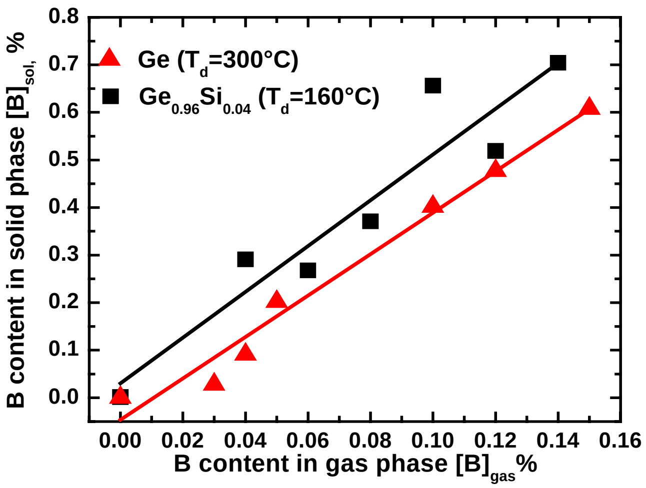


Figure 2 Boron solid content dependence on gas content in deposition process for LT $Ge_{0.96}Si_{0.04}$:H films with fit slope $k_{LTB}=4.8 \pm 0.7$ and HT Ge:H films with fit slope $k_{HTB}=4.3 \pm 0.2$.

The incorporation of phosphorus from gas phase to solid phase in $Ge_{0.96}Si_{0.04}$ doped films is shown in figure 3. The best fit for LT $Ge_{0.96}Si_{0.04}$:H films in the range of $[P]_{gas}$= 0.04 to 0.22 % describes the incorporation as $[P]_{sol}= k_{LTP}[P]_{gas}$($k_{LTP} = 2.77 \pm 0.02$) and for HT Ge:H is described by $[P]_{sol}= k_{HTP}[P]_{gas}$ ($k_{HTP}= 3.5 \pm 0.3$)

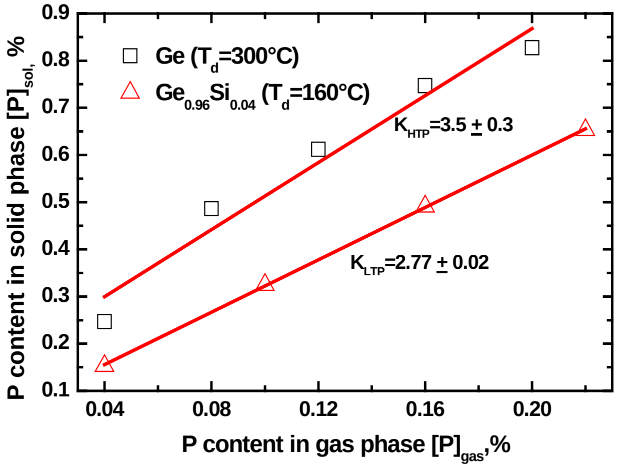
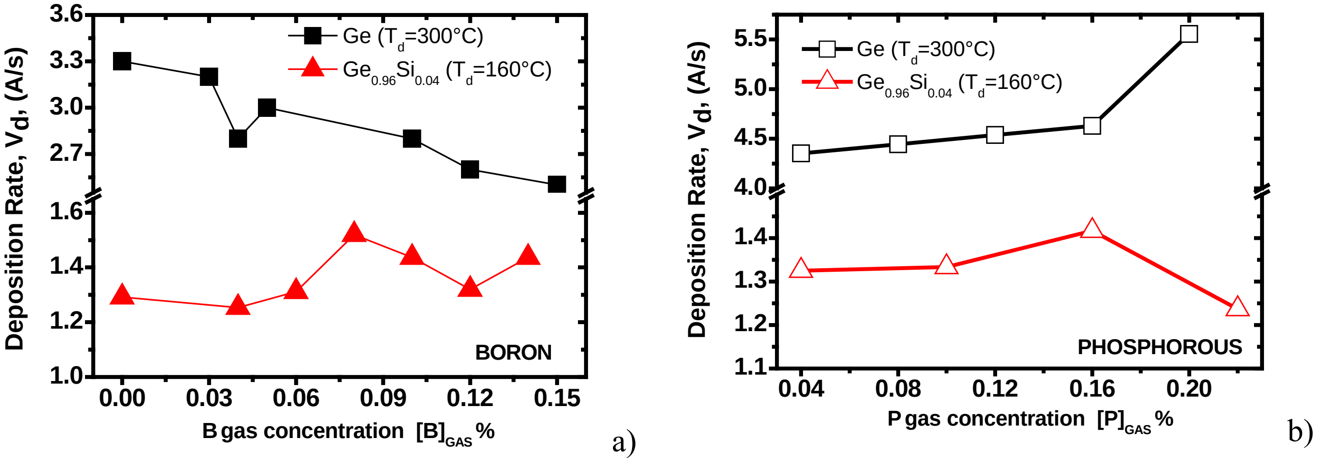


Figure 3 Phosphorus solid content dependence on gas content in deposition process for LT $Ge_{0.96}Si_{0.04}$:H films with fit slope $k_{LTP} = 2.77 \pm 0.02$ and HT Ge:H films with fit slope $k_{HTP}= \pm 0.35 \pm 0.02$

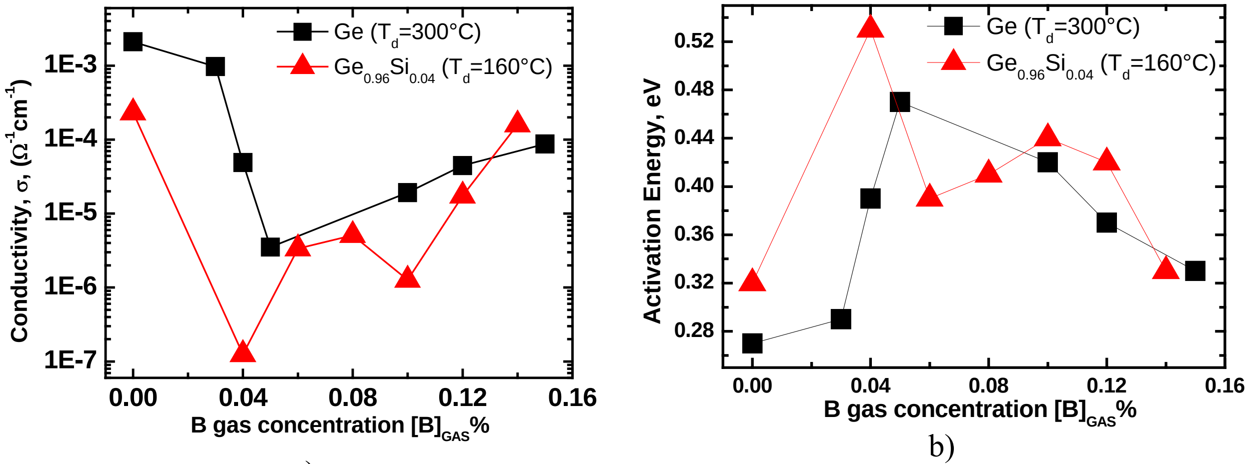
The figure 4 shows deposition rate for boron in LH and HT samples. In the range studied for Ge:H films deposition rate changed from V_{dHT}=2.5 to 3.3 A°/s and for LT $Ge_{0.96}Si_{0.04}$ films deposition rate changed slightly in the range from V_{dLT}=1.2 to 1.4 A°/s. For HT Ge:H doped with phosphorus deposition rate varied in the range of V_{dHT}=4.3 to 5.5 A°/s and for LT films in the range V_{dHT}=1.3 to 1.4 A°/s. The deposition rate ratio for intrinsic films is $V_{ratio}=V_{dHT}/ V_{dLT}$= 2.5.



a) b)

Figure 4 Deposition rate as a function of a) boron and b) phosphorus concentration for Ge films deposited at T_d=300°C and $Ge_{0.96}Si_{0.04}$ films deposited at T_d=160°C.

The electrical characteristics for boron doped films are shown in figure 5. For LT room temperature conductivity σ_{RT} shows a drastically reduction from $\sigma_{RT}= 10^{-4}$ to 10^{-7} Ω^{-1} cm^{-1} with increasing boron from $[B]_{gas}$= 0 to 0.04% and further increasing from $[B]_{gas}$=0.04 to 0.14% results in increase of conductivity from $\sigma_{RT}= 10^{-7}$ to 10^{-4} Ω^{-1} cm^{-1}. For HT films σ_{RT} decreases from $\sigma_{RT}= 10^{-3}$ to 10^{-6} Ω^{-1} cm^{-1} in the range of $[B]_{gas}$ = 0 to 0.05% and in the range of $[B]_{gas}$= 0.05 to 0.15% the conductivity shows increase from $\sigma_{RT}= 10^{-6}$ to 10^{-4} Ω^{-1} cm^{-1}. Both cases suggest a compensation of electron conductivity in un-doped film. The compensation effect has relation with the activation energy maxima at HT with E_a=0.46 eV for $[B]_{gas}$=0.05% and LT with E_a=52 eV for $[B]_{gas}$=0.04%.



a) b)

Figure 5 a) Conductivity and b) activation energies as function of boron concentration in gas phase for HT Ge and LT $Ge_{0.96}Si_{0.04}$ films.

The electrical characteristic for phosphorus doping is shown in the figure 6. For LT films changes of $[P]_{gas}$ from 0.04% to 0.22% resulted in more than 2 orders increasing conductivity and reducing activation energy from E_a=0.24 to 0.18 eV. HT films in same range are demonstrated saturation of conductivity with change in one order of magnitude. Both HT and LT films showed continuous reducing E_a with increase of $[P]_{gas}$.

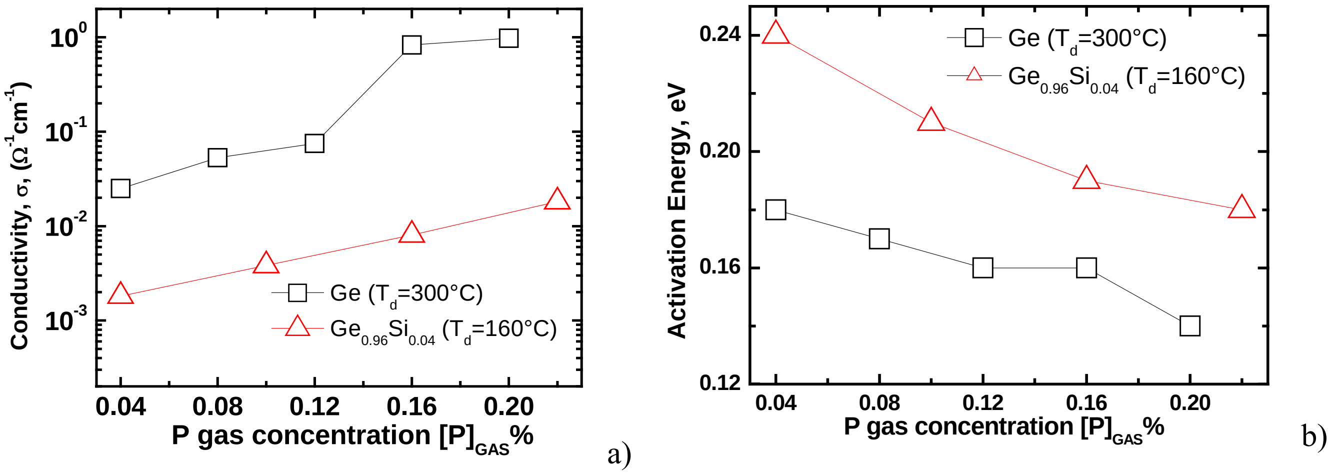


Figure 6 a) Conductivity and b) activation energy as function of phosphorus concentration in gas phase for HT Ge:H and LT $Ge_{0.96}Si_{0.04}$:H films.

CONCLUSIONS

The main parameter affected by temperature is deposition rate for both HT and LT films doped with boron and phosphorus. In Ge:H and $Ge_{0.96}Si_{0.04}$ films no effect of deposition temperature was observed on boron incorporation from gas phase into solid phase in the samples deposited at temperature T_d=300 and 160°C. Electrical characteristics of Ge:H and $Ge_{0.96}Si_{0.04}$ are similar and both HT and LT samples demonstrated compensation effect around $[B]_{gas}$=0.05%. Lower phosphorus incorporation was observed in LT Ge:H films in comparison with HT films. This is also reflected in the electrical characteristics following the incorporation of phosphorus. The reduction of incorporation of phosphorus decreases conductivity and increase E_a for LT $Ge_{0.96}Si_{0.04}$ films in comparison with those for HT Ge:H films.

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