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# Thin film GaP for solar cell application

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**Abstract.** A new approach to the silicon based heterostructures technology consisting of the growth of III-V compounds (GaP) on a silicon substrate by low-temperature plasma enhanced atomic layer deposition (PE-ALD) is proposed. The basic idea of the method is to use a time modulation of the growth process, i.e. time separated stages of atoms or precursors transport to the growing surface, migration over the surface, and crystal lattice relaxation for each monolayer. The GaP layers were grown on Si substrates by PE-ALD at 350°C with phosphine (PH<sub>3</sub>) and trimethylgallium (TMG) as sources of III and V atoms. Scanning and transmission electron microscopy demonstrate that the grown GaP films have homogeneous amorphous structure, smooth surface and a sharp GaP/Si interface. The GaP/Si heterostructures obtained by PE-ALD compare favourably to that conventionally grown by molecular beam epitaxy (MBE). Indeed, spectroscopic ellipsometry measurements indicate similar interband optical absorption while photoluminescence measurements indicate higher charge carrier effective lifetime. The better passivation properties of GaP layers grown by PE-ALD demonstrate a potential of this technology for new silicon based photovoltaic heterostructure

## 1. Introduction

Silicon based solar cells are by far dominating the PV market due to the availability and relatively low price of Si substrates. One of the most efficient ways to increase the Si solar cell performance is to use heterojunction designs. Thus heterojunctions combining hydrogenated amorphous silicon (a-Si:H) and crystalline silicon (c-Si) have reached 24.7% conversion efficiency for n-type Si wafers with conventional architecture, and 25.6% when combined with interdigitated back contacts [1]. Thin layers of a-Si:H deposited by PECVD at temperature below 250 °C with a gap of 1.65-1.75 eV provide an excellent passivation of the c-Si surface with relatively low light absorption in a-Si:H. An increase of the Si heterojunction solar cell efficiency could be achieved by further reducing the absorption in the emitter layer using a material with a higher band gap. On the other hand a-Si:H/c-Si heterojunctions are not so successful for p-type Si wafers, which are still of interest for low orbit space applications due to better radiation hardness [2].

GaP could fit both requirements as a wide gap emitter. GaP has a gap of 2.26 eV and has the smallest lattice mismatch beyond III-V binary compounds (less 0.4 %) providing conditions for low defect density at the interface with the Si substrate [3]. Therefore, GaP/Si heterojunctions are of great interest for photovoltaic applications, which according to simulations give an advantage of more than 1% of efficiency compared to passivated emitter and rear cells made of p-type Si wafers [4]. However,



the commonly used techniques for the growth of GaP layers such as molecular beam epitaxy (MBE) and metal organic vapor-phase epitaxy (MOVPE) require high temperatures of 800-900°C at least at the initial stage for silicon oxide removing and surface reconstruction [5-9]. High temperatures affect the Si wafers quality and the properties of III V/Si interface leading to low photovoltaic performance of GaP/Si heterojunctions obtained by epitaxy compared to the high efficiency a-Si:H/c-Si solar cells [10, 11]. The problem can be related to elastic stresses in the growing layer, which lead to the appearance of dislocations. This problem is associated primarily with the high temperatures required for the growth due to different coefficients of thermal expansion in silicon and GaP. More-over, the use of high temperatures leads to inter-diffusion of group-III and -V atoms into Si and opposite, which act as dopants affecting the electrical properties of heterojunctions, and it can also promote the fast diffusion of species that can degrade the carrier lifetime in c-Si [12]. In this paper we propose to use a new technological approach for the growth of III-V compounds on Si substrates using low temperatures (less than 400°C) and plasma-enhanced atomic layer deposition (PE-ALD). This technique consists of alternatively changing the phosphorus and gallium atom source flows providing the growth of one monolayer by cycle.

## 2. Experiment

3 inch p-type silicon substrates with a doping level of  $10^{16} \text{ cm}^{-3}$  and (100) orientation ( $4^\circ$  cut-off towards (110)) were used for GaP deposition. At the initial stage the native oxide was removed from the Si surface by HF-dip (10%) immediately before the growth of the GaP layer. The time between HF dip and deposition start does not exceed 30 min.

The PE-ALD deposition was performed using the Oxford Plasmalab 100 PECVD (13.56 MHz) setup supplied with phosphine ( $\text{PH}_3$ ) and trimethylgallium (TMG) lines for sources of phosphorus and gallium, respectively. Hydrogen was used as a gas carrier for TMG. The hydrogen pressure was 3 bar while the temperature of the TMG cylinder was kept at 3°C.

Three different deposition modes were used: i) continuous PECVD mode (sample # 1) with  $\text{PH}_3$  and  $\text{TMG}/\text{H}_2$  flows of 50 sccm, RF power of 5 W, gas pressure  $P = 250 \text{ mTorr}$  and deposition time of 7.5 min with growth rate of about 8 nm/min; ii) ALD mode where  $\text{PH}_3$  and  $\text{TMG}/\text{H}_2$  flows were alternatively changed with continuous plasma discharge due to Ar flow addition during the purge step (samples #2, 3); iii) ALD mode with plasma interruption, evacuation and purge steps (sample # 4). In this case in order to provide reliable plasma ignition at each growth step the higher RF power (50 W) was used and Ar was added to the  $\text{TMG}/\text{H}_2$  flow. The deposition parameters for ALD modes are given in table 1. All ALD processes consist of 50 cycles. The substrate temperature of 350°C was the same for all the processes.

Epitaxial single-crystal GaP layers grown by MBE [10] on Si substrates from the same batch were used as reference samples.

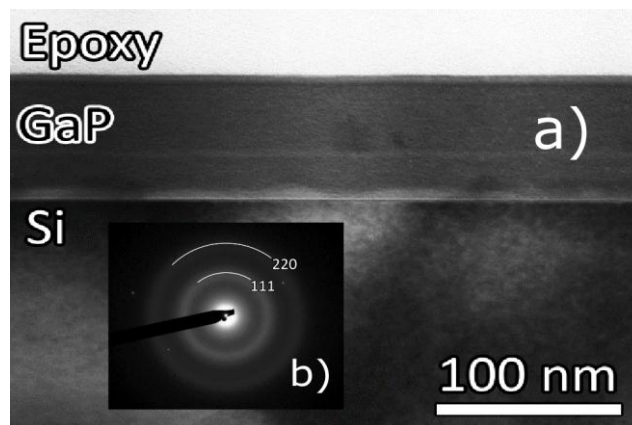
**Table 1** Deposition parameters of the four samples.

Step	ALD mode with continues plasma		ALD mode with plasma interruption
	Sample # 2	Sample # 3	Sample # 4
P step	$\text{PH}_3=50 \text{ sccm}$ $t = 10 \text{ s}$ $P = 250 \text{ mTorr}$ RF=5 W		$\text{PH}_3=50 \text{ sccm}$ $t = 5 \text{ s}$ $P = 250 \text{ mTorr}$ RF=50 W
evacuation	None		$t = 20 \text{ s}$ $P < 0.1 \text{ mTorr}$
purge	Ar =50 sccm $t = 10 \text{ s}$ $P = 250 \text{ mTorr}$ RF=5 W	Ar =50 sccm $t = 20 \text{ s}$ $P = 250 \text{ mTorr}$ RF=5 W	Ar =30 sccm $t = 10 \text{ s}$ $P = 250 \text{ mTorr}$
Ga step	$\text{TMG}/\text{H}_2=50\text{sccm}$ $t= 10\text{s}$ $P=250\text{mTorr}$ RF=5W		$\text{TMG}/\text{H}_2= 50 \text{ sccm}$ Ar =30 sccm $t = 5 \text{ s}$ $P = 250 \text{ mTorr}$ RF=50 W
Thickness per cycle	~1.6 nm	~1 nm	~1.3 nm

### 3. Results

#### 3.1. Structural properties

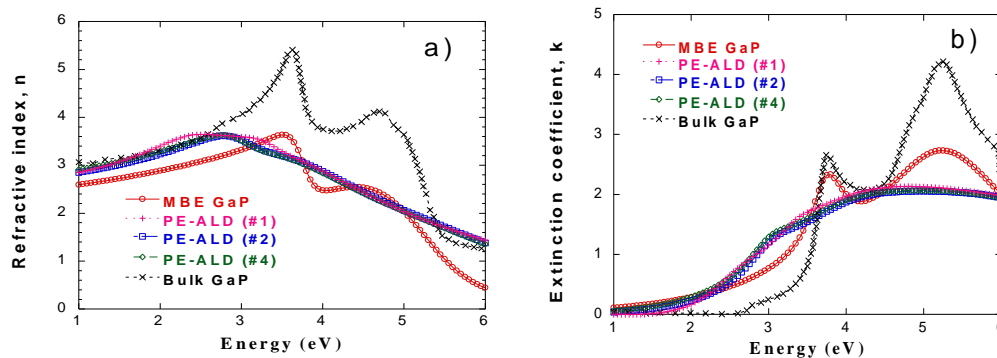
The layer morphology and thickness were determined using scanning electron microscopy (SEM) (SUPRA 25 Zeiss). The grown GaP films have homogeneous structure and smooth surface. The RMS roughness measured by AFM is in the range of 0.2-0.3 nm. The structural properties were studied by transmission electron microscopy (TEM) (Philips EM420). An example of TEM images for the PE-ALD GaP layer is presented in Figure 1. TEM demonstrates a sharp GaP/Si interface. The selected area electron diffraction (SAED) pattern of the GaP film obtained by TEM (inset of Figure 1) shows a dominant amorphous phase.



**Figure 1** TEM photography of cross section (a) and HEED pattern (b) of PE-ALD GaP layer (sample #2).

#### 3.2. Optical properties

Ellipsometric angles  $\Psi$  and  $\Delta$  were measured using spectral ellipsometer Uvisell 2 (Horiba Scientific). The measurement range was from 0.6 to 6.5 eV with a step of 0.05 eV. An estimation of refractive index ( $n$ ) and extinction coefficient ( $k$ ) was performed in terms of Bruggeman effective medium approximation “BEMA” [13]. The spectra were simulated in approximation of isotropic substrate/isotropic layer obtaining a good agreement with experimental data. GaP dispersion was set in the approximation of four harmonic oscillators (quatre amorphous) [14]. Optical properties of GaP layers grown by PE-ALD were compared with ones of GaP grown on Si by MBE [10] (Figure 2). Also  $n$  and  $k$  spectra of bulk GaP [15] are presented in Figure 2 for the reference. The general behaviour of  $n$  and  $k$  spectra for MBE GaP is similar to that of bulk GaP with the same peaks positions. The difference in absolute values could be caused by the low thickness (<200 nm) of the MBE GaP layer. On the contrary the behaviour of PE-ALD GaP  $n$  and  $k$  spectra differs from that of the bulk GaP. The peaks are unclear and their positions are shifted. This difference is obviously due to band structure changes of amorphous GaP. However the absorption of PE-ALD GaP does not exceed that of MBE GaP for photon energy less than 2.3 eV indicating low interband absorption of PE-ALD GaP. This is an essential issue for the photovoltaic structures which require to minimize absorption in the wide gap emitter GaP layer.

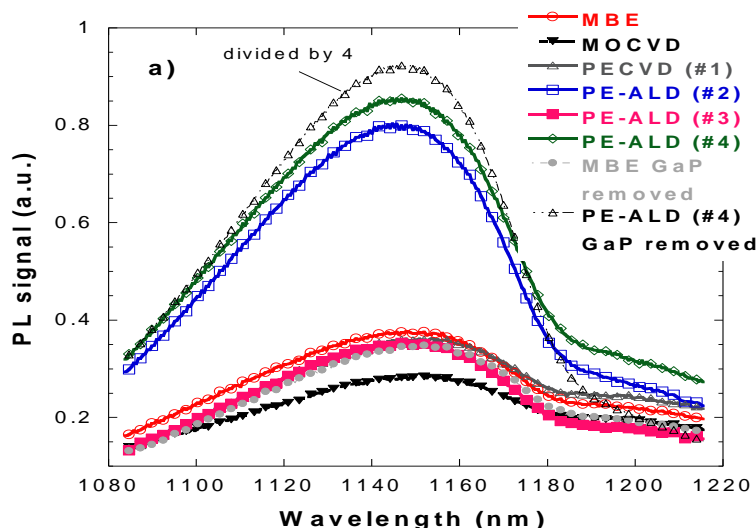


**Figure 2** Experimental refractive index (a) and extinction coefficient (b) determined from spectroscopic ellipsometry for GaP layers on Si grown by MBE and PE-ALD.

### 3.3. Passivation properties

Photoluminescence is known to be a powerful tool for the characterization of interface properties in Si based heterojunctions [16,17]. The radiative recombination of excess carriers in the volume depends on the effective lifetime, which is affected by surface recombination. The signal of the PL from Si (at  $\lambda=1150$  nm) decreases with increasing recombination rate at the GaP/Si interface. The photoluminescence (PL) measurements were performed at room temperature with excitation at 778 nm wavelength (minimum absorption in GaP) using Accent RPM Sigma PL.

The PL spectra for the series of the GaP/Si samples fabricated using PECVD technology are presented in Figure 3a. Also the PL spectra for the MBE layers are shown. The back side of all the samples was passivated by a thin a-Si:H layer in the same process to avoid any influence of the back interface. The intensity of PL signal for the samples #2 and #4 obtained in ALD mode is significantly higher compared to epitaxial GaP/Si structures indicating considerable improvement of the Si surface passivation. Low PL signal for the sample #3 is obviously caused by double Ar plasma time. Ar plasma, which was used to keep the discharge during gas exchange, is known to create radiation defects and to reduce charge carrier lifetime in Si. The sample #1 obtained in continuous mode exhibits low PL intensity.



**Figure 3** Photoluminescence spectra for MBE, MOCVD, PECVD and PE-ALD GaP/Si heterostructures

## 4. Discussion

The fact that PE-ALD provides better passivation of Si wafers compared to MBE technology is encouraging. We should stress that initially all the Si substrates were similar (with the same charge

carrier lifetime). However high temperatures of MBE processes could lead to higher defect density in Si substrates, due for instance to rapidly diffusing defects into the Si wafer [12]. On the contrary low temperature PE-ALD process should not affect the properties of Si wafers. To verify this difference the GaP layer was removed by wet etching (acid based etchant) for MBE and PE-ALD (#4) grown samples followed by silicon surface passivation. The intensity of PL signal (Figure 3a) for MBE sample remained at the same level while for the PE-ALD sample the PL intensity increased by factor of four being 70% of the PL signal from initial Si wafer passivated by a-Si:H (not presented). This fact clearly indicates the silicon degradation during the high temperature MBE growth. The 30% difference between PL signal for Si wafer at initial state and after PE-ALD GaP layer removing is associated with radiation defects. The decrease of PL signal with Ar plasma time demonstrates that Ar addition should be rather avoided. The hydrogen will be used in further technology development.

The difference for the samples obtained in continuous and ALD modes indicates the sensitivity of Si passivation quality to growth conditions and GaP layer properties. Therefore there is still a room for improvement when further detailed study using in particular high resolution TEM will be performed.

## 5. Conclusion

GaP layers were grown on Si substrates by PE-ALD at 350°C. The grown GaP films have homogeneous amorphous structure, smooth surface and a sharp GaP/Si interface. The proposed PE-ALD provides better passivation properties of GaP/Si heterostructures, which does not deteriorate Si wafer, compared to MBE demonstrating a high potential of this technology for new silicon based photovoltaic heterostructures that has to be confirmed by further development of the proposed technology (including a doping facility) and layer properties study.

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