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CVD boron containing glasses - an attractive alternative diffusion source for high quality emitters and simplified processing - A review

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Abstract

This review presents the current state of the art and interesting questions with regard to CVD BSG layers. The advantages of CVD doping sources over the conventional $POCl_3$ and BBr_3 or BCl_3 gaseous sources are the simple way to deposit a diffusion source on only a *single* side of the wafer and structuring the diffusion source to achieve dopant concentration profiles next to each other on the same side of the wafer. In addition, these CVD glasses are multifunctional. The same CVD BSG can serve e. g. as doping source, passivation layer, antireflective coating and as electrical insulator.

Monofacial n-type solar cells achieve efficiencies up to 20.5% on a 156 x 156 mm^2 n-type Cz-Si solar cell. Bifacial cells of that size show efficiencies up to 20.1%. Back junction back contact cells show an efficiency of 20.5% on 4 cm^2 aperture area.

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Keywords: CVD; BSG; multi-purpose layer; doping source; surface passivation

1. Introduction

Boron silicate glasses (BSG) deposited by atmospheric pressure (AP) and plasma enhanced (PE) chemical vapor deposition (CVD) have a long tradition in microelectronics in particular as a combination with P in BPSG (B,P silciate glass). Only recently CVD BSG and PSG layers were entering photovoltaics widely as diffusion source for

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solar cells of different design. As early as 1991 one of the first applications of APCVD PSG on solar cells was published [1].

The advantages of CVD doping sources over conventional POCl3 and BBr3 or BCl3 gaseous sources are the simple way to deposit a diffusion source on only a single side of the wafer and structuring the diffusion source to achieve dopant concentration profiles next to each other on the same wafer side. Also throughput for diffusion might be enhanced since in particular wafers receiving B doping can be put closer to each other in the furnace yielding an uniform and tailored doping profile. This implies further advantages for process developments as co-diffusion of B and P from different sources: either from different CVD glasses or from one dopant containing CVD glass and a conventional dopant from gas phase. Implantation of dopants, which is also a single side method for dopant deposition and can be combined in a co-diffusion, is out of scope of this review.

The focus of this review lies on the manifold applications and studies of CVD BSG for Si solar cells. In particular n-type Si solar cells use CVD BSG as a diffusion source with additional benefit due to the multi-purpose properties of the dopant containing layer as surface passivation and contact formation support [2].

Since B concentration in the BSG is in the percent range and the resistance of a less than 100 nm thick CVD BSG layer is in the tera-Ohm range, as determined using an electrometer, the BSG is not called B doped but B containing here.

2. Deposition methods for CVD-BSG

The most widely applied CVD methods are APCVD and PECVD, whereas the latter splits up into remote plasma with microwave plasma (MW) source and inductively coupled plasma (ICP) PECVD, and those with a PECVD plasma source which is not further specified. In microelectronics also low pressure (LP) CVD and catalytic (CAT) CVD was applied [3]. The deposition methods use different precursor gases as O, P and B sources, e.g. O2, N2O and CO2 as oxygen source, diborane in hydrogen or nitrogen and TEB (triethylboron) as B source, silane and TEOS (tetraethylorthosilicate) as Si source.

2.1. APCVD

Most APCVD depositions of BSG use B_2H_6 in N_2, SiH_4 and O_2 as precursor gases. If a capping layer is needed, SiO_X is deposited from SiH_4 and O_2 [4, 5]. Deposition temperatures tend to be higher than for PECVD due to the deposition method whereas throughput is in general higher since no vacuum needs to be established. With APCVD either a B layer was deposited with a subsequent drive-in in oxidizing atmosphere [6], or a silicate glass containing about 4 wt% B [7].

The saturation current density of APCVD B emitters j_{0e} was determined to below 55 fA/cm^2 with an atomic layer deposited AlO_X surface passivation layer [5]. Further, Schiele *et al.* observed an increase in sheet resistance with decreasing SiO_X capping layer thickness after $POCl_3$ co-diffusion (B drive in N_2 atmosphere) in parallel with an increase in j_{0e} [5]. Based on electrochemical capacitance voltage (ECV) profiles showing an increased net doping with increased capping layer thickness, it was concluded that the number of P atoms reaching the Si surface decreases for thicker capping layers [5].

Rothhardt *et al.* [8] also investigated the influence of capping layer thickness on the electrically active B concentration in Si. In contrast to Schiele *et al.* [5] they used an oxidizing, O_2 containing, B drive-in atmosphere. When reducing the SiO_X capping layer thickness from 200 nm to 100 nm, the Si surface is stronger oxidized and the B surface is reduced. However, the profile with the thicker capping layer is at a concentration of 1×10^{17} cm^{-3} about 75 nm less deep than the profile with thinner capping. Comparing this behavior with another investigation of Rothhardt *et al.* [8], it seems that the profile with the thick capping layer shows a similar depth dependence as one with a boron rich layer (BRL) despite the fact that a BRL is not visible in the profile with thick capping layer.

2.2. PECVD

Already in 2009, Cabal *et al.* [9] investigated a diffusion from a 660 nm thick CVD BSG layer using a direct PECVD at 480°C with TEOS and TEB as precursor gases for a BSG also stating that a certain time between CVD BSG deposition and drive-in changes sheet resistance.

The influence of the delay between deposition and drive-in might be due to the incorporation of water vapor from ambient air as also suspected by Tanvir *et al.* [4] whereas Keding *et al.* investigated this issue and demonstrated that keeping a BSG from a PECVD microwave plasma with SiH_4, N_2O B_2H_6 as precursor gases for 2 weeks in ambient air has no influence on the sheet resistance [10].

For BSG layers from ICP-PECVD it was demonstrated that they at least serve two purposes at once with only a single layer/stack (SiN_X:H capping) as dopant source and surface passivation [2]. The precursor gases were SiH_4, B_2H_6 in H_2 and CO_2. j_{0e} of about 50 fA/cm^2 for an emitter of 80 Ω/sq sheet resistance was achieved by using its own dopant source layer as passivation layer [2], *i.e.* there was no detrimental BRL formed during the deposition process and the B drive-in atmosphere was N_2 only. The reference sample passivated with a non-fired Al_2O_3/SiN_X:H stack showed a value of about 30 fA/cm^2 [2]. Another PECVD method used for the deposition of such multi-purpose layers is the microwave plasma source. Here a stack of 5 nm AlO_X and 200 nm B-doped amorphous Si was deposited and used as passivation layer leading to a saturation current of 47 fA/cm^2 at a sheet resistance of 280 Ω/sq [11].

Keding *et al.* [10] investigated the dependence of the sheet resistance on BSG thickness (MW PECVD, SiH_4, N_2, B_2H_6). For a BSG thickness above 200 nm, the sheet resistance of about 50 Ω/sq. did not decrease with increasing BSG thickness anymore.

For BSG from ICP-PECVD it was demonstrated that the BSG can be as thin as 10 nm providing still an emitter that could be contacted at a low contact resistivity with conventional Ag/Al pastes. With a BSG layer of 30 nm and 100 nm thickness, the B emitter could be contacted with a contact resistivity of 1 mΩcm^2 using commercial Ag paste usually applied to highly phosphorous doped areas of a solar cell [2].

The influence of capping layer thickness was investigated using a MW-PECVD system and the following precursor gases: SiH_4, B_2H_6 and N_2O for BSG and SiH_4, N_2O and Ar for the SiO_X capping [4]. The thicker the capping layer (in the range of up to 110 nm), the lower the resulting sheet resistance [4], which was assumed to be an effect of absorption of humidity in the BSG which reduces B diffusion and might be stronger in case the capping layer is thinner [4]. Since no P was available in this process, the reason cannot be an overcompensation as in the case investigated by Schiele *et al.* [5].

Wehmeier *et al.* simulated a diffusion profile generated from a BSG source deposited by ICP-PECVD using SiH_4, B_2H_6 and N_2O as precursor gases. They detected a small difference in diffusion profile comparing a BBr_3-based diffusion with the one from a CVD BSG [12, 13]. Investigation of the B concentration profile within the CVD BSG showed for optimum PECVD parameters with regard to solar cell efficiency an increased concentration at the interface to Si. Averaged B concentrations of ICP-PECVD with CO_2 as oxygen source are slightly higher than those from N_2O as precursor gas. The range of B concentration in the CVD BSG is 4-9 × 10^{-21} cm^{-3} [2, 13]. In both cases deposition parameters were found avoiding a BRL.

3. Boron rich layer

In 2009, Cabal *et al.* [9] published the dependence of sheet resistance on the B concentration in the BSG formed by a PECVD tool. At a B concentration between 4 and 5 wt%, the sheet resistance reaches its minimum and for higher B concentration the sheet resistance increases again slightly. In 2012 the same behavior was observed by Kurachi and Yoshioka for an APCVD BSG [7]. They [14] found that at a B concentration of 4.28% in the BSG a BRL was formed as can be deduced from a profile measuring the chemical concentration of B atoms. Kurachi and Yoshioka identified the BRL to be responsible for a shallower B profile for increasing B concentration in the CVD-BSG above 4.65 × 10^{21} cm^{-3} [15].

A qualitative explanation says that up to the B concentration in the BSG needed for BRL formation the enhanced diffusivity of silicon-boron interstitial pairs compared to single B atoms leads to higher diffusivities, deeper B profiles, and thus lower sheet resistances when comparing different BSG under the same diffusion process [14]. When the B concentration is high enough that a BRL is formed, *i.e.* SiB_X molecules, the availability of Si interstitials for the formation of silicon-boron pair interstitials is reduced and thus the enhancement of the diffusivity is reduced leading to less deep profiles. Kurachi and Yoshioka also developed an analytical model to describe B diffusion from an APCVD BSG [15, 16, 17] including the effect of the BRL. For the determination of the diffusivity, three different types of diffusion were considered: intrinsic, surface concentration and local concentration dependent diffusion [15]. With those diffusivities, Kurachi and Yoshioka modeled profiles with and without BRL accurately.

Such a BRL is highly recombinative and should be avoided when the same CVD BSG shall be used as passivation layer after the dopant drive-in. There are two different approaches possible: either deposition of a BSG that does not support a BRL, or an additional O_2 atmosphere during B drive-in to prevent the formation of BRL.

Both approaches were demonstrated, however the latter has up to now not proven to allow for passivating BSG layers.

4. Co-diffusion

Co-diffusion using a CVD PSG as P source needs a lot of attention regarding P concentration in the CVD PSG to generate suitable P depth profiles while being at high temperature to form the B-profile [18]. Optimization of the P profile is not dealt with in this review.

Currently mainly two types of co-diffusion processes using $POCl_3$ as P source are used. Rothhardt *et al.* [8] run during B drive-in also a $POCl_3$ process to obtain a deep P profile, and at a lower temperature a second $POCl_3$ diffusion is carried out to increase P surface concentration to achieve low contact resistivities for screen-printed contacts. Another process uses only one $POCl_3$ diffusion during cool down after the B drive-in *e.g.* [13, 19].

While most investigations of a co-diffusion concentrate on how to avoid an inter-diffusion of P and B in Si, Gloger *et al.* [20] looked also at the P and B depth profile in Si when diffusing in both elements together to gain information on the interaction of the diffusing species.

In case of a $POCl_3$ diffusion at 832°C for 44 min and a BSG layer of 27 nm thickness, the P depth profile is not affected by the thin BSG. The B profile in contrast is completely overcompensated and shows a convex form due to the strong reduction of B diffusivity in the P kink region [20].

When going to higher temperatures as used for B drive-in (temperature 920°C, duration 100 min) and investigating the influence of P found on the walls of the $POCl_3$ tube on the B profile from a BSG layer of 73 nm thickness and the P profile, interesting results were found. When comparing the P profile (no $POCl_3$, just P from the tube walls) on wafers with and without the BSG layer, the P profile on wafers with BSG is much deeper and higher in concentration [20]. The explanation here was that the BSG has a low glass transition and flow temperature which leads to a high diffusivity of P in the BSG. In addition, the BSG dissolves more P than a bare Si wafer [20].

This effect can be used to generate three differently doped regions in one step. *I.e.*, for a back junction back contact (BJ-BC) solar cell, a light $POCl_3$ diffusion can generate a front surface field while a heavy P profile can be formed in areas where a BSG can take in P from the tube walls, and a capped BSG generates a B doped region. The highly P doped region in the uncapped area beneath the BSG was explained by an integrated diffusion model based on known dependences of diffusion constants on dopant concentrations [21].

5. Solar cells

Besides the diffusion processes and surface passivation, contact formation is an important process step. Investigations from Frey *et al.* [22] showed the challenges occurring when contacting B emitters by screen-printed Ag/Al paste. The detrimental effect of Al spiking should be overcome. A possible approach was demonstrated by

Engelhardt *et al.* [2], demonstrating low contact resistivities of 1 mΩcm^2 by applying conventional Ag paste, normally used to contact P emitters, also to B emitters.

5.1. n-PERT

PERT cells (passivated emitter and rear totally diffused) on n-type Si material processed using a CVD BSG as emitter dopant source in a co-diffusion process with $POCl_3$ or a PSG as P source can be found in monofacial or bifacial version. For the bifacial approach, Cabal *et al.* presented an average efficiency of 19.8% for $POCl_3$ and 19.9% for PSG as P source, respectively. The highest cell efficiency was 20.1%.

Table 1. Solar cell parameters of bifacial solar cells manufactured using a CVD BSG and two different P doping sources for a co-diffusion process [23].

	V_{OC} [mV]	J_{SC} [mA/cm^2]	*FF* [%]	η [%]
SOLENNA(1) $POCl_3$/BSG	648	39.7	77.2	19.8
SOLENNA(2) PSG/BSG	648	38.8	79.1	19.9

Monofacial cells are produced with a full area Al rear metal that locally contacts the B emitter. The Al layer might be screen-printed or deposited by physical vapor deposition. The former approach led to efficiencies of up to 21.0% [24] while 20.5% on a 156 x 156 mm^2 n-type Cz-Si were achieved using the latter approach [25].

5.2. n-PERT

In particular for BJ-BC solar cells which need at least three different types of diffused regions (lightly doped front surface field, heavily doped back surface field and B doped emitter), the application of CVD glasses as dopant source is attractive. Keding et al. [26] and Tanvir et al. [4] developed PECVD BSG and PSG layers as well as POCl3 co-diffusion parameters for the fabrication of BJ-BC solar cells with an efficiency of 20.5% (independently confirmed) on a cell size of 4 cm2 (aperture area). As in the case of bifacial solar cells, CVD PSG and POCl3 served as P doping source and led to the same efficiencies.

Table 2. Solar cell parameters of BJ-BC solar cells manufactured using a CVD BSG and two different P doping sources for a co-diffusion process [4, 26].

Dopant source FSF/Emitter/BSF	V_{OC} [mV]	J_{SC} [mA/cm^2]	*FF* [%]	η [%]
$POCl_3$/BSG/PSG [4] 4 cm^2 (designated area)	656	40.5	77.2	20.5
PSG/BSG/PSG [26] 4 cm^2 (designated area)	659	40.9	76.0	20.5

6. Conclusion

Single side deposited CVD-dopant containing glasses have clear advantages when used for solar cell processing, CVD BSG can serve as a multi-purpose layer. *e.g.* as doping source and simultaneously as surface passivation layer and antireflection coating. Nevertheless, more detailed investigation is necessary to better understand the interplay of deposition parameters and glass properties on a basis of bonding structure and resulting doping profile.

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