HOLE COLLECTING CONTACTS BY Pt WITH PtSi FORMATION

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ABSTRACT: By applying an external negative drift field source for the creation of a p-conduction layer doping can be spared apart from the hole collection contact where p^+ doping has to be done. If a metallic layer of sufficiently high electron work function is used a p^+ contact can be formed as well. Platinum (Pt) is a perfect candidate for such a contact. Unfortunately its performance is limited by the current crowding effect occuring at the edges as the space charge of a Schottky contact is rather small.
However, with an area of high electron work function and conductivity underneath the Pt contact the diffusion current flows perpendicular into that region. Platinum Silicide (Pt_xSi) is a material which fulfills these requirements. It is synthesized by depositing Pt onto a Silicon (Si) substrate and subsequent anneal. In this paper we present experimental results and discuss advantages and drawbacks of such a contact design.
Keywords: Contact – 1: Sputtering – 2: Interfaces – 3

1 INTRODUCTION

The contact to an n inversion layer of an MIS (n-IL-MIS) solar cell is realized by using Titanium or Aluminium (Al) as a conductive material with a low electron workfunction [1]. This Schottky contact does not represent a good current path in itself due to the current crowding effect [2]. For that reason an ultrathin Siliconoxynitride (SiO_xN_y) layer with a fixed positive charge is grown prior to Al evaporation. That fixed positive charge accelerates electrons over the insulating barrier whereby tunneling becomes the major transport regime [3]. The second task of the SiO_xN_y layer is a passivation of the silicon (Si) surface at the contact such that the surface recombination rate approaches zero [4].

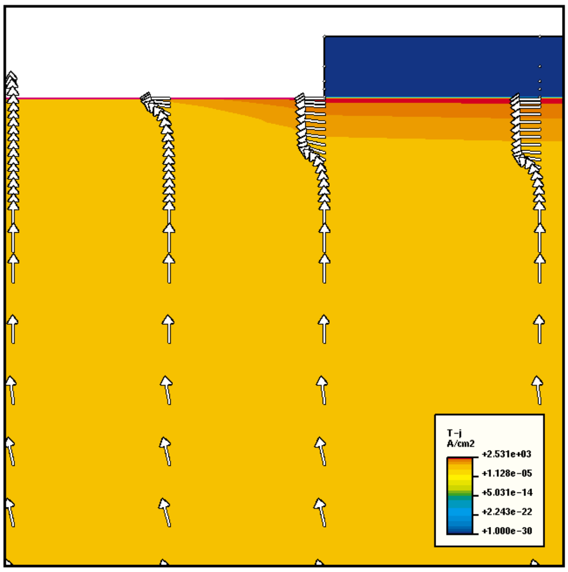

Figure 1: Current crowding effect underneath a Schottky type Pt / p-Si contact to a p accumulation layer induced by the I^-S structure. The area shown is $(1 \times 1)\ \mu m^2$. Simulations were carried out by DESSIS / TCAD 6.0 [9].

Recently, a so-called I^-S structure with an effective fixed charge of $N_{eff} \approx -4 \times 10^{12}\,cm^{-2}$ and anti-reflective properties was introduced [5, 6, 7, 8]. It employs Aluminiumfluoride (AlF_3) and can be deposited onto Si. The drift field generated thereby is on the order of $\vec{F}_{drift} = -6 \times 10^5\,Vcm^{-1}$ at the Si surface. With help of the I^-S structure p inversion layer solar cells on n type Si are feasible. In analogy to the MIS contact at the n-IL-MIS solar cell a metal with a very high electron workfunction (E_{WF}) has to be employed for getting a good hole collecting contact. Metals of the Pt group, especially Pt itself, possess the properties required. Unfortunately the melting temperature of Pt group metals is very high (e.g. T_{melt}(Pt)= 1774 °C). Hence the only way for Pt deposition is sputtering which in return does not allow for any intact ultrathin insulation layer underneath Pt. As expected the Schottky contact Pt / Si suffers from the current crowding effect as well. Fig. 1 shows the simulation of a current flow in a p accumulation layer towards a Pt-like electrode ($E_{WF} = 5.21\,eV$).

2 Pt CONTACT FOR P CONDUCTION LAYERS

2.1 Contact Design

If Pt is sputtered onto Si and exposed to a Hydrogen (H_2) tempering process subsequently, much of the radiation damage is annealed and Platinum Silicide (Pt_xSi, x =1 . . . 2) is formed. Table 1 shows some relevant material parameters of Pt_xSi.

Silicide	electrical behaviour	ϱ [$\mu\Omega$cm]	φ_{Sch} [eV]	substr.
Pt_2Si	metallic	30 - 35	+0.85	n-Si
PtSi	metallic	28 - 35	+0.88	n-Si
PtSi	metallic	28 - 35	+0.21	p-Si

Table 1: Electrical characteristics, specific resistance ϱ, band bending of the Schottky space charge region φ_{Sch} on respective substrate for Pt_xSi [10, 11].

Pt_xSi possess a high E_{WF} such that positive band bending is induced even on p type Si. Due to the conductive area extending into the Si substrate the diffusion current density vector $\vec{J}_{diff}(p)$ runs perpendicular to the interface Pt_xSi / Si. Therefore current crowding is avoided. For that reason the Pt_xSi formation can be exploited as p conductive material for solving the problem of current crowding as shown in Fig. 2.

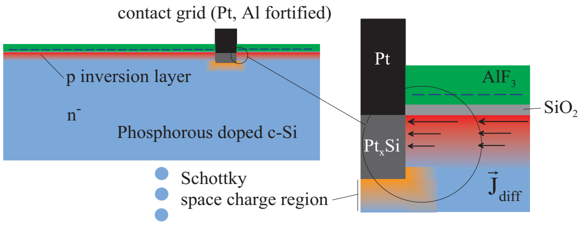

Figure 2: Principle of contact design for avoiding current crowding by introducing a Pt_xSi layer underneath the Pt contact; $\vec{J}_{diff}(p)$ flows perpendicular to Pt_xSi / Si

2.2 Experimental

Phosphorous doped 2.2 Ωcm Si wafers of 4” diameter, majority carrier life time $\tau_n \approx 50\,\mu s$ (”test grade”) and <100> surface orientation were used as substrate. After initial cleaning (RCA process) and HF-Dip for removing native SiO_2 the wafers were oxidized by Rapid Thermal Oxidation (RTO) to a thickness of $d_{SiO_2} = 20$ Å or $d_{SiO_2} = 68$ Å. Onto the oxidized samples 300 nm Pt was deposited in a magnetron sputtering system (HZM, VEB Elektromat) with a sputtering power ($P_{sputter}$) of 200 W or 500 W. Dots of 1.1 mm diameter and an intermediate distance of 5 mm were prepared by employing vapour masks during sputtering. Afterwards the samples were annealed in H_2 at $T = 550\,°C$ for $t = 5$ min. Table 2 presents the sample data.

Tansmission Electron Microscopy (TEM) characterization and Electron Energy Loss (EELS) Spectroscopy were performed by a PHILIPS CM-20. I-V measurements were carried out with an AVT-110 tester and a KEITHLEY 236 source measure unit.

sample	d_{SiO_2}	d_{Pt}	$P_{sputter}$
	[Å]	[nm]	[W]
A	68	300	500
B	68	300	200
C	20	300	200

Table 2: Data of samples prepared

2.3 Results

Fig. 3 shows the crystallographic structure of sample C around the SiO_2 layer. The <110> Si lattice plains are clearly visible. First monolayers of SiO_2 can be seen as a thin dark strip on top of Si. The Thickness of the remaining SiO_2 layer is 9 Å. It merges into an amorphous transition layer with a thickness of about 15 Å.

An EELS image of exactly the same region gives a more detailed look onto the distribution of O, Pt and Si. Obviously the SiO_2 layer is severely damaged.

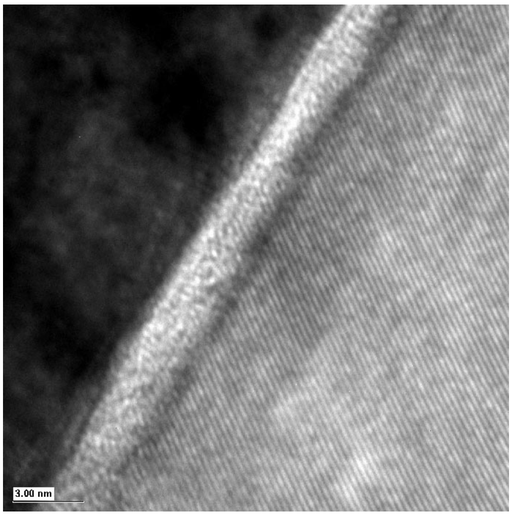

Figure 3: high resolution TEM image of sample C around the SiO_2 layer.

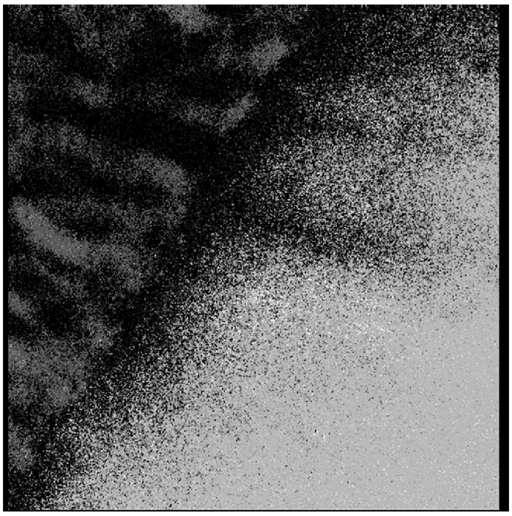

Figure 4: EELS mapping of sample C, same area as in fig. 3; black = O, grey = Pt, light grey = Si.

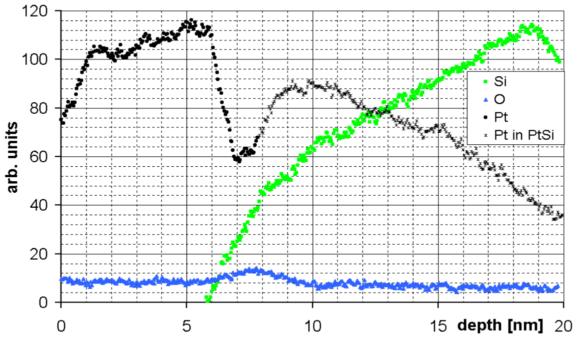

Figure 5: EELS profile of sample C along an orthonormal cut through the structure of fig. 4. Lateral integration of values was done over a width of ±62.5 Å around the cut. Due to different cross sections the O signal is underrepresented.

Both O and Pt are spread into Si as can be seen in fig. 4.

Integrating EELS values of respective elements along an orthonormal line to the layers yields a more representative distribution of O, Pt and Si is obtained. The lateral line thickness was chosen to be 125 Å. In Fig. 5 the profile is shown.

The Pt concentration breaks down at the interface SiO$_2$ / Pt as expected. However, it is increasing beyond the interface SiO$_2$ / Si. These Pt atoms have formed Pt$_x$Si, $x = 1 \ldots 2$.

Pt$_x$Si formation is promoted by annealing. Pt$_2$Si is formed in a metastable phase at $T = 250 \ldots 300\,°\mathrm{C}$ [12]. A reaction Pt$_2$Si $\longrightarrow$ PtSi takes place at $T = 400 \ldots 500\,°\mathrm{C}$ for ultraclean Pt. In our case Pt contains some O so that both Silicide phases coexist. For Pt containing O the onreaction occurs around $T = 800\,°\mathrm{C}$ in a fairly short reaction time of $t = 10 \ldots 15\,\mathrm{s}$ [13, 14].

On all three samples I-V curves of the contacts to bulk Si were measured as shown in fig. 6. They could be clearly identified as Schottky type.

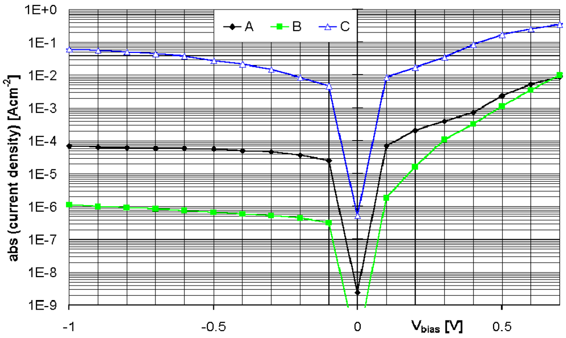

Figure 6: Typical dark I-V curves of respective samples

3 DISCUSSION

Some basic equations shall give a rough description of the Schottky type contacts. A more detailed evaluation is given in [10].

The field induced at the interface Pt$_x$Si / Si is given by

$$\vec{F}_{Sch} = -\sqrt{\frac{2\,q\,N_{dope}\,\psi_{Sch}}{\varepsilon_0\,\varepsilon_{Si}}} \qquad (1)$$

whereby

$$\psi_{Sch} = \frac{k\,T}{q}\,\ln\left(\frac{n(x = d_{SCR})}{n(x = 0)}\right) \qquad (2)$$

with ψ_{Sch} being the band bending over the Schottky SCR, N_{dope} as the doping density of the base (assumed to be n type) and d_{SCR} as the extension of the space charge region (SCR) . For moderate base doping of $N_{dope} = 10^{16}\,\mathrm{cm}^{-3}$ $\vec{F}_{Sch}$ is on the order of $50\,\mathrm{kVcm}^{-1}$. The Schottky space charge is given by

$$Q_{SCR} = \varepsilon_0\,\varepsilon_{Si}\,\vec{F}_{Sch} \qquad (3)$$

and is about $Q_{SCR} = 3.4 \times 10^{11}\,\mathrm{cm}^{-2}$. The depth of the SCR,

$$d_{SCR} = \sqrt{\frac{2\,\varepsilon_0\,\varepsilon_{Si}\,\psi_{Sch}}{q\,N_{dope}}} \qquad (4)$$

is $d_{SCR} \approx 340\,\mathrm{nm}$ for the assumptions mentioned above.

Due to the formation of Pt$_x$Si underneath the Pt contact current crowding can be prevented since $\vec{J}_{diff}$ is orthonormal to the interface Si / Pt$_x$Si as depicted in fig. 2. That leads to a lower serial resistance in comparison to conventional MIS or Schottky contacts. As Pt$_x$Si exposes a metallic behaviour the contact interface is practically shifted from Pt into Si. Hence a high density of dislocations within the Si lattice and also thermally inactive dopands introduced by formation of a highly doped p type area are circumvented. There is also no band gap narrowing induced by p$^+$ doping. So recombination losses and reduction of the open circuit voltage (V_{OC}) due to these effects can be eliminated.

The behaviour of a Schottky contact is goverened by majority carriers [10]. For that reason $\vec{F}_{Sch}$ and Q_{SCR} are pretty low although $\psi_{Sch} \approx 0.88\,\mathrm{eV}$. The absence of majority carriers (electrons) within the Schottky SCR gives way to an increased majority carrier diffusion current towards the barrier. These mayority carriers recombine within the Schottky SCR, leading to an additional loss. Their diffusion length is an order of magnitude lower than d_{SCR} foe the conditions stated above. Thereby the dark current is high, see also fig. 6. These conditions apply to the interface Pt$_x$Si / n-Si of the bulk only.

For the p conduction layer $\psi_{Sch} \approx 0$ because of the high density of holes. So in the enlargement of fig. 2 an ohmic contact for hole collection exists. At the interface of Pt$_x$Si to the p conduction layer the density of electrons is somewhat low due to an external negative drift field source or due to a high level p type doping. There the effective surface recombination velocity (S_{eff}) drops to very low values. However, in case of doping the doping density has to be chosen with care as the blue response of the cell deteriorates and the recombination rate (R) increases if the doping density gets too high [15].

Beyond the interface Pt$_x$Si / Si the two quasi Fermi levels (E_{F_n}, E_{F_p}) collapse immediately at $E_F(\mathrm{Pt}_x\mathrm{Si})$. Therefore S_{eff} within Pt$_x$Si is very high so that holes recombine massively with electrons from Pt$_x$Si as desired for a hole collecting contact of a solar cell. It should be noted again that the actual contact interface is Pt$_x$Si / Si and *not* Pt / Pt$_x$Si.

Decreasing d_{SiO_2} and increasing $P_{sputter}$ (= increasing Pt ion energy) enhance the deposition of Pt in Si and thus the subsequent formation of Pt$_x$Si during H$_2$ anneal. If d_{SiO_2} is big enough (samples A and B) an MIS contact exists with Pt$_x$Si underneath SiO$_2$. However, the SiO$_2$ quality is very low due to radiation damage what leads to very poor diode characteristics as can be seen in fig. 6.

In summary, there is a trade-off between the Schottky SCR towards bulk n-Si which is prone to high R and the ohmic contact of the p inversion layer to Pt$_x$Si. The losses within the Schottky SCR represent a shunt resistance parallel to the hole collecting contact. Judging from the dark I-V charactristics in fig. 6 the recombination loss in the Schottky SCR clearly outweights the contact gain for the p inversion layer.

4 CONCLUSIONS

In our paper we evaluated the possibility of preparing a hole collecting contact by using Pt as a contact material in analogy to Al / SiO_2 / n-Si structures for collecting electrons. In contrast to Al-MIS contacts the use of Pt creates a highly conductive Pt_xSi area of high E_{WF} underneath SiO_2 after an H_2 anneal. Thereby the current crowding effect can be eliminated. Due to its high T_{melt} the only economical way to deposit a metallic phase of Pt is sputtering. However, the sputtering of Pt induces heavy radiation damage to the SiO_2 layer. Hence the SiO_2 quality is very poor, resulting in a Schottky rather than an MIS contact.

According to our measurements the high R within the Schottky SCR clearly outweights the gain given by the elimination of the current crowding effect. In summary we conclude that Pt as material for a hole collection contact for solar cells cannot be recommended.

Acknowledgements

The author wishes to thank Dr. Schulze from the Institute of Physics, Technical University of Chemnitz for TEM and EELS characterization.

REFERENCES

[1] M.A. Green, A.W. Blakers, J. Shi, E.M. Keller, S.R. Wenham, IEEE Tr. on ED **31**, 679 (1984)

[2] B. Kuhlmann, M. Grauvogl, R. Meyer, R. Hezel, G. Heiser, A.G. Aberle, 14th European PVSEC, Barcelona/Spain, 1997, Proc. pp. 2465

[3] M.A. Green, F.D. King, J. Shewchun, Solid State Electronics **17**, 551 (1974)

[4] C. Leguijt, P. Lölgen, J.A. Eikelboom, A.W. Weeber, F.M. Schuurmans, W.C. Sinke, P.F.A. Alkemade, P.M. Sarro, C.H.M. Marèe, L.A. Verhoef, Solar Energy Materials & Solar Cells **40**, 297 (1996)

[5] D. König, G. Ebest, Sol. St. Electron. **44**, 111 (2000)

[6] D. König, M. Rennau, M. Henker, G. Ebest, Thin Sol. Films **385**, 126 (2001)

[7] D. König, G. Ebest, OC 9.3, 12th Int. PVSEC, Cheju/Korea, 2001, Proc. pp. 285

[8] D. König, R. Scholz, S. Gemming, I. Thurzo, T.U. Kampen, D.R.T. Zahn, G. Ebest, Int. Workshop on Nanostr. in PV, Max-Planck-Inst. Phys. of complex Systems, Dresden/Germany, July 28 - August 4 2001

[9] $TCAD_{ISE}$ 6.0 manuals, ISE AG Zürich/Switzerland, 1999

[10] K.W. Böer, *Survey of semiconductor physics, Vol. II (Barriers, junctions, surfaces and devices)*, Van Nostrand Reinhold, New York, 1992

[11] K. Maex, M. van Rossum (eds.): Properties of Metal Silicides, EMIS datareview series **14**, INSPEC publications, 1995

[12] J.Van der Spiegel, C.S. Wei, J.J. Santiago, J. Appl. Phys. **57**, 607 (1985)

[13] V.E. Borisenko, D.I. Zarovskii, V.P. Lesnikova, Poverkhnost **4**, 96 (1989)

[14] A.K. Pant, S.P. Murarka, , C. Shepard, W. Lanford, J. Appl. Phys. **72**/5, 1833 (1992)

[15] M.A. Green, A. W. Blakers, IEEE Tr. on Electron. Dev. **30**, 1360 (1983)