ELECTROCHEMICAL INVESTIGATIONS OF SILICON/BORON PHOSPHIDE HETEROJUNCTION PHOTOELECTRODES

A. GOOSSENS* and J. SCHOONMAN

Delft University of Technology, Laboratory for Applied Inorganic Chemistry, Julianalaan 136,
2628 BL Delft, The Netherlands

(Received 20 December 1994)

Abstract—An electrochemical study of Si/BP heterojunction photoelectrodes was undertaken in order to explore the feasibility of utilizing such electrodes in liquid junction solar cells. It appears that in the case of *n*-type Si/*n*-type BP heterostructures, only low photocurrent densities are produced by the electron-hole pairs generated in the wide-bandgap BP window. In contrast, *p*-type Si/*n*-type BP heterojunctions show large cathodic photocurrents upon irradiation with visible light. Detailed impedance analysis was carried out to derive the band diagrams of the two studied configurations. It appears that an excellent match between the conduction bands of Si and BP is present, which explains the observed effects. In addition, surface trapping and recombination phenomena at the BP/electrolyte interface were explored with impedance techniques.

Key words: boron phosphide, heterojunctions, photoelectrodes.

INTRODUCTION

It has been known for some decades that thin films of boron phosphide, BP, can be grown epitaxially onto silicon substrates by using gas-phase deposition techniques[1]. In fact, large area single crystalline wafers of BP can only be obtained by chemical vapour deposition (CVD) growth of BP and subsequent etching of the silicon substrate[2]. The laborious procedure of producing BP wafers has caused this so-called III–V semiconductor material to be one of the least studied members of its class. This, however, discredits the great potential of BP as semiconductor material. Since both boron and phosphorus are commonly employed as dopants for silicon, BP is a refractory compound, *ie* fully compatible with the silicon industry.

Another property of boron phosphide is the low mass of its constituent elements, which makes it the lightest III–V compound with semiconductor properties. Cubic BP crystallizes in the usual zincblende structure with a lattice parameter of 453.83 pm[3]. BP crystals are extremely chemically inert and resist all conventional etchants. Moreover, the Vickers hardness of BP resembles that of TiN, which makes BP suitable as a ceramic hardcoating material[4]. Cubic BP has an indirect optical bandgap of 2.0 eV[5] and the first direct optical transition occurs at approximately 5.0 eV[6]. As expected, excess of B produces *p*-type and excess of P *n*-type material.

In this paper, the photo-electrochemistry of Si/BP heterojunction semiconductor electrodes are dis-

cussed. In 1983, Ginley, Baughman and Butler[7], aiming at an efficient and durable device for solar energy conversion, studied Si/BP heterojunction photoelectrodes. In their investigations, degenerate *n*-type epitaxial BP was employed as a protective optical window on *n*-type Si and *n*-type GaAs substrates. Hence, their device basically resembles a metal-coated semiconductor electrode in which the semiconductor properties of BP are fully disregarded. In our investigations this is not the case since we were able to grow non-degenerate *n*-type epitaxial boron phosphide films on both *n*-type and *p*-type silicon substrates. We could determine the flat-band potential of BP from detailed Mott–Schottky analysis by which the position of the conduction and valence band with respect to those bands of Si were derived. In addition, also charge trapping and recombination in electronic surface states at the BP/electrolyte interface were examined in some detail.

EXPERIMENTAL ASPECTS

Epitaxial films of BP on Si substrates were obtained by chemical vapour deposition (CVD) using a cold-wall reactor with radio-frequency inductive substrate heating. The Si substrates were (100) oriented and had resistivities of about 0.1 Ω cm, corresponding to a doping density of 10^{17} cm⁻³. The reactants used were BBr₃ and PBr₃ and hydrogen was employed as carrier gas. The heterogeneous reaction takes place at 900°C. Under these conditions, BP films grow with a rate of about 1 μ m per hour. Usually the deposition time was chosen to be 1/2 h so that films of 0.5 μ m thickness were studied.

* Author to whom correspondence should be addressed.

The electrochemical experiments were carried out in a conventional 3-electrode electrochemical cell with optical access through a quartz window. A large-area platinum sheet was used as counter electrode and a saturated calomel electrode (*sce*) served as potential reference. The following aqueous indifferent electrolytes were used of which the pH varies between 1 and 13; (0.1 M) H_2SO_4 , (0.05 M) H_2SO_4 + (1 M) KCl , (0.05 M) HAc + (0.05 M) NaAc + (1 M) KCl , (0.1 M) $\text{Na}_2\text{B}_4\text{O}_7$ + (1 M) KCl , (0.1 M) KOH . A high-pressure Xe lamp in combination with a monochromator and high-pass cut-off filters provided monochromatic irradiation. The intensity of this irradiation was calibrated with a thermopile. Photocurrent and impedance analysis were performed mostly in either (0.1 M) H_2SO_4 and (0.1 M) KOH . Photocurrent action spectra were recorded with low-frequency (5 Hz) chopped light and lock-in detection. There is no observed dependence of the photocurrent on the composition of the electrolyte. Voltage control and current measurement were handled by a potentiostat (Solartron Model 1286) and impedance analysis was carried out by a network analyzer of the same supplier (Model 1250). Details on the experimental conditions were published previously[8].

RESULTS AND DISCUSSION

Current-voltage analysis

Current-voltage curves, both in the dark and under illumination for both *n*-type Si/*n*-type BP and *p*-type Si/*n*-type BP heterojunctions are shown in Fig. 1a and 1b, respectively. As can be seen in those figures, in both cases the dark current resembles that

Fig. 1. Current-voltage characteristics of *n*-Si/*n*-BP (a) and *p*-Si/*n*-BP photoelectrodes (b). The solid line corresponds to the dark current and the dashed line to the combined dark and photocurrent.

of an *n*-type semiconductor electrode. Upon irradiation, however, the two heterostructures show a remarkably different photocurrent response. As is shown in Fig. 1a, *n*-Si/*n*-BP electrodes show anodic photocurrents with densities in the order of a few $\mu\text{A cm}^{-2}$. In contrast, *p*-Si/*n*-BP electrodes show large cathodic photocurrent densities with an order of magnitude of 10 mA cm^{-2} (Fig. 1b). Obviously, two quite different mechanisms must be active to account for those observed differences in sign and, more remarkable, the difference in magnitude of the photocurrent densities of four decades. In order to explore these mechanisms, photocurrent action spectra were recorded using monochromatic irradiation. Again, a completely different behaviour is observed between the two studied electrode configurations as is shown in Fig. 2a and 2b. In the case of *n*-Si/*n*-BP (Fig. 2a), the anodic photocurrent shows a threshold excitation energy at 2.0 eV, whereas in the case of *p*-Si/*n*-BP (Fig. 2b) a threshold energy of 1.1 eV is found. These values clearly agree well with the optical bandgaps of BP and Si, respectively. This agreement is more convincingly demonstrated by the so-called Fowler plots (Figs 3a and 3b) as constructed from Figs 2a and 2b. For the case of *n*-Si/*n*-BP, the a plot of $(QY E_{ph})^{1/2}$ vs. E_{ph} , where QY is the quantum yield and E_{ph} the photon energy, shows a linear region that extrapolates to 2.0 eV. In contrast, for the case of *p*-Si/*n*-BP heterojunctions, a similar plot extrapolates to 1.1 eV. Accordingly, the optical bandgaps of BP and Si are exactly reproduced from

Fig. 2. Quantum yield (QY) spectra of *n*-Si/*n*-BP (a) and of *p*-Si/*n*-BP (b) heterostructures. The quantum yield is defined as the photocurrent density divided by the flux of incoming irradiation.

Fig. 3. Fowler plots as constructed from the data of Figs 2a and b. In plot (a) *n*-Si/*n*-BP, and in (b) *p*-Si/*n*-BP heterostructures are investigated as photoelectrodes.

the photocurrent action spectra. In addition to the bandgap values, also the indirect nature of the optical bandgaps of both BP and Si are nicely confirmed by the linearity of the $(QY E_{ph})^{1/2}$ vs. E_{ph} plots.

These observations strongly suggest that in the case of *n*-Si/*n*-BP electrodes, the anodic photocurrents are the result of electron-hole pair generation in BP, whereas in the case of *p*-Si/*n*-BP, electron-hole pairs generated in Si are responsible for the cathodic photocurrent. The fact that in the first case the anodic photocurrent is four orders of magnitude smaller than the cathodic photocurrent in the second case can be explained from the thickness of the BP films of only 0.5–1.0 μm compared to the 300 μm thick Si wafers in conjunction with the indirect nature of the optical band-to-band transition. The BP film only absorbs a small fraction of the incident irradiation whereas the Si substrate absorbs all impinging photons with sufficient energy.

The question that naturally arises now is why, for *n*-Si/*n*-BP electrodes, the photons with energy between 1.1 and 2.0 eV and the fraction of the photons with energy larger than 2.0 eV that pass the BP phase are apparently unable to produce a photocurrent. No doubt, electron-hole pairs are being generated in Si by these photons, but some reason must prevent them contributing to the photocurrent. In order to answer this question, a detailed impedance analysis of both systems was carried out.

Impedance analysis

By measuring the impedance over a wide frequency span as function of the applied *dc* voltage,

one can derive the flat-band potential of BP and compare this to the flat-band potential of Si. These flat-band potentials can subsequently be related to the positions of the conduction band and valence band edges of BP and Si, and a band diagram of the heterostructure can thus be obtained. The procedure runs as follows: a *dc* voltage is applied between the working electrode and the calomel reference and after a short stabilization period of a few seconds an impedance spectrum is recorded. Subsequently, the voltage is stepped to the next value *etc.* The thus obtained collection of impedance spectra is fitted to a well chosen electrical equivalent circuit. This circuit has to comply to the following two requirements

- (i) it must model the frequency response of the system accurately at every applied frequency and
- (ii) the equivalent circuit must be the same for every applied voltage with only the values of the circuit elements changing.

The equivalent circuit that fulfils these requirements is presented in Fig. 4. In this figure, R_s is the series resistance of the wires and the electrolyte, R_F is the Faradaic resistance that accounts for the *dc* current flow across the BP/electrolyte interface, C_{sc} is the space charge capacitance of BP, and $R_1C_1, \dots, R_3C_3$ represents charge trapping in surface states as will be further discussed shortly. By virtue of this procedure, the circuit elements do not possess any frequency dependency and have values that are functionally related to the applied voltage.

A Mott-Schottky plot of C_{sc}^{-2} vs. V is constructed from the collection of C_{sc} values. For ideal Schottky barriers, such plots are linear as is the case with our electrodes. For both systems, *ie* *n*-Si/*n*-BP and *p*-Si/*n*-BP, similar Mott-Schottky plots are obtained and a typical example with KOH (1 M) as electrolyte is shown in Fig. 5. The Mott-Schottky relation reads

$$C_{sc}^{-2} = (2/\epsilon\epsilon_0 e N_D A^2)(V - \Phi_{fb} - kT/e)$$

where, ϵ is the relative dielectric constant, ϵ_0 is the permittivity, e is the elementary charge, N_D is the donor density, A is the surface area, Φ_{fb} is the flat-band potential, k is the Boltzmann constant, and T is the absolute temperature. The slope of a C_{sc}^{-2} vs. V plot equals $2/\epsilon\epsilon_0 e N_D A^2$ from which a value of N_D can be obtained. In our case an effective donor density of $5 \times 10^{19} \text{ cm}^{-3}$ was found. Linear extrapolation to the potential axis gives an intercept of

Fig. 4. The equivalent circuit that is used to model the impedance of both types of electrodes. The values of the circuit elements are a function of the applied voltage.

Fig. 5. Mott-Schottky plot of C_{sc}^{-2} vs. V of both types of studied electrodes. The electrolyte was KOH (1 M) and the surface area was 7.1 mm^2 .

$V_0 = \Phi_{fb} + kT/e$, from which a reliable value for the flat-band potential can be derived.

By choosing distinct (buffered) indifferent electrolytes with pH ranging from 1 to 13 it was found that Φ_{fb} shows the well-known pH dependency of -60 mV per decade. Accordingly, the flat-band potential of BP in indifferent aqueous electrolytes is found to be $\Phi_{fb} = (-0.27 - 0.06 \text{ pH}) V$ vs. *sce*.

Next, a value for the distance between the Fermi level and the conduction-band minimum of BP is needed. Both, thermal conductivity and thermopower, *ie* Seebeck coefficient, measurements can provide this information. The two techniques both led to a value of about 50 meV .

Only now we are in a position to calculate the positions of the conduction band and valence band of BP at the BP/electrolyte interface vs. the calomel reference. These positions are, $E_c = (0.32 + 0.06 \text{ pH}) \text{ eV}$ vs. *sce*, and $E_v = (-1.68 + 0.06 \text{ pH}) \text{ eV}$ vs. *sce*, where the experimental accuracy is approximately 50 meV . The pH for which the surface concentration of H^+ equals that of OH^- species is at $\text{pH} = 6.4$ as was derived with the method proposed by Ginley *et al.*[9]. The conduction and valence band positions of silicon were determined by others following more or

less the same procedure[10]. It must be noted, however, that the values given by these authors differ somewhat due to the fast formation of an insulating SiO_2 film onto Si in aqueous solutions. This rapid passivation complicates Mott-Schottky analysis and gives some uncertainty in the exact flat-band potential. Nevertheless, it is found from Mott-Schottky analysis that the conduction bands of both Si and BP match in energy with a difference of less than about 0.1 eV . As a consequence, the valence bands of the two materials must differ by approximately 0.9 eV in the sense that the wider bandgap material BP has a valence band maximum that lies 0.9 eV deeper in energy compared to this band maximum of Si. In Fig. 6 the band diagrams of *n*-Si/*n*-BP and *p*-Si/*n*-BP are sketched.

What happens upon irradiation is the following. In the case of *n*-Si/*n*-BP heterojunctions, irradiation with $h\nu > 1.1 \text{ eV}$ generates electron-hole pairs in Si, but since there is only little band bending at the Si/BP interface, the driving force for charge separation is small. Moreover, in order to produce anodic photocurrents, the photoholes need to flow either into the valence band of BP or recombine with conduction-band electrons. The first possibility is virtually absent because of the large energy barrier of 0.9 eV that the photoholes need to pass. The second possibility may occur, but in this case subsequent electron injection from the electrolyte into the conduction band of BP is required, which is an unlikely process when indifferent electrolytes are present. All in all, both the lack of sufficient driving force in combination with energy barriers that need to be passed, suppress the flow of anodic photocurrents in *n*-Si/*n*-BP heterojunction photoelectrodes. Only photons with energy $> 2.0 \text{ eV}$ may generate electron-hole pairs in BP. At sufficient anodic potentials, a space charge region builds up at the BP/electrolyte interface and provides a driving force for charge separation. In this case, both the photoelectrons and the photoholes do not face any appreciable potential barriers and charge flow may thus occur. Consequently, anodic photocurrents coming from BP can be observed in these heterostructures but photocurrents originating in Si are absent.

With *p*-Si/*n*-BP heterojunctions a completely different situation exists. In this case, an electric field is built into the junction which bends the bands of primarily Si and forms a driving force for charge separation. When electron-hole pairs are generated in Si, the photoelectrons may cross the Si/BP inter-

Fig. 6. Band diagrams of *n*-Si/*n*-BP and *p*-Si/*n*-BP heterojunctions. The redox potentials of H^+/H_2 and OH^-/O_2 are 4.5 and 5.73 eV below vacuum, respectively.

Fig. 7. Schematic representation of the influence of the externally applied voltage on the band bending in Si/BP heterojunctions. As can be seen, the band bending in Si near the Si/BP junction is unaffected by the external voltage, whereas the band bending of BP at the BP/electrolyte interface is voltage dependent.

face without having to mount an energy barrier because of the excellent match of the conduction bands. The injected electrons subsequently flow towards the BP/electrolyte interface where they do face an energy barrier unless the band bending in this region is removed. A negative applied voltage is thus required and only when V is close to Φ_{fb} cathodic photocurrents are possible.

The band diagrams as drawn in Fig. 6 explain not only the observed i - V curves in the dark and upon illumination, but also the photocurrent action spectra and the impedance behaviour. Despite the relative ease with which these diagrams could be derived, it has the power of explaining at least three independent observations and, therefore, must be a fairly accurate representation of the electronic structure of these heterojunctions.

To make this discussion complete, a phenomenon implicit in the followed argumentation needs to be addressed. Upon applying an external voltage, the bands in BP at the BP/electrolyte interface are bent. Applied voltage differences apparently drop at this interface rather than at the Si/BP interface. This was confirmed by the following observations. First, we note that Mott-Schottky plots at both n -Si/ n -BP and p -Si/ n -BP electrodes are identical. This would certainly not be the case if the applied voltage would distribute itself over the two phase boundaries. Secondly, by applying electrical ohmic contacts on the BP surface it was confirmed that almost linear i - V curves were obtained from which a small resistance was derived. Consequently, externally applied voltages do not drop at the Si/BP interfacial region. The actual situation is schematically presented in Fig. 7, where changes of the band bending of BP are depicted at different externally applied voltages.

Surface states

Surface states on BP in contact with indifferent electrolytes manifest themselves through one or more parallel RC branches in the electrical equivalent circuit. It appears that Si/BP electrodes left in inorganic acids for a prolonged time show very pronounced surface trapping phenomena. The space-charge capacitance has been degraded into a so-called constant phase element (*cpe*) as defined in [11]. The power factor lies between 0.8 and 0.9 so that the *cpe* shows a similarity with an ordinary

capacitance. The prefactor K , derived from the *cpe*, is almost equivalent to C_{sc} and is plotted vs. V for aged Si/BP electrodes in acid electrolyte in Fig. 8. A typical local maximum occurs which can be deconvoluted from the space-charge capacitance after making a Mott-Schottky plot of K^{-2} vs. V (Fig. 9) and subtracting the space-charge capacitance contribution obtained by interpolation between the two linear regions. The followed procedure is discussed in more detail in [12]. The result is that the space-charge capacitance appears to add up with C_1 and C_2 of the equivalent circuit (Fig. 4), and that the $R_3 C_3$ branch could not be observed with sufficient accuracy in this case (but they are present in other, more alkaline, electrolytes). The observation that C_1 and C_2 adds up with the space charge capacitance can be explained from the presence of small resistances R_1 and R_2 . In case that $R_1 \ll 1/\omega C_1$ and $R_2 \ll 1/\omega C_2$ for all applied frequencies the two resistors can be neglected and may be removed from the equivalent circuit (Fig. 4). In this case, the parallel capacitors add up to one sum-capacitor and the

Fig. 8. K vs. V for aged Si/BP photoelectrodes in acid electrolytes.

Fig. 9. Mott-Schottky plot of K^{-2} vs. V constructed from the data of Fig. 8.

equivalent circuit reduces to a resistor, R_s in series with a parallel combination of R_F and the sum-capacitor.

The distorted C_{sc} shows a typical Mott-Schottky behaviour but is shifted cathodically on the potential axis. The $C_1 + C_2 = K_{ss}$ obtained after subtraction of C_{sc} from K is presented in Fig. 10. This figure shows two maxima from which both the density and the energetic position of the surface states can be derived. In our case, surface state densities of 2.2×10^{12} and $5 \times 10^{11} \text{ cm}^{-2}$ are found at 0.68 and 0.96 eV below the conduction-band edge, respec-

Fig. 10. $C_1 + C_2 = K_{ss}$ as a function of the applied voltage. Two maxima can easily be deconvoluted from which the density and location of surface states on BP surfaces in contact with acid electrolytes can be derived.

tively. The argument is further elaborated in [12] and the capacitance of surface trapping and recombination is discussed in [13] to which the interested reader is referred.

SUMMARY AND CONCLUSIONS

The following conclusive remarks can be made. In the first place the measured flat-band potential of BP indicates that the conduction bands of Si and BP show an excellent match. Band diagrams for n -type Si/ n -type BP and p -type Si/ n -type BP could be constructed and proved to explain the i - V curves, the photocurrent action spectra, and the impedance behaviour. Externally applied voltages were noted to drop only at the BP/electrolyte interface and not at the Si/BP junction. Large cathodic photocurrents can be observed at p -Si/ n -BP electrodes and this heterojunction can thus be used as an efficient photoelectrode for regenerative photovoltaic devices provided that the chosen redox couple has a rather negative redox potential. For instance the V^{2+}/V^{3+} or the $\text{Eu}^{2+}/\text{Eu}^{3+}$ couples seem suitable as we were able to confirm for the first couple. Surface states on BP at BP/electrolyte interfaces are present with rather high densities in acid electrolytes. The pH of the solution should thus be kept high to reduce surface recombination losses.

Acknowledgements—The Royal Netherlands Academy of Arts and Sciences is kindly acknowledged for the grant that secured continued research of Dr. A. Goossens and led to this publication.

REFERENCES

1. K. Shohno, H. Othake and J. Bloem, *J. Crystal Growth* **45**, 187 (1978).
2. Y. Kumashiro and Y. Okada, *Appl. Phys. Lett.* **47**, 64 (1985).
3. Landolt-Börnstein, Group III, Vol. 17a, Springer-Verlag, Berlin (1982).
4. E. M. Kelder, A. Goossens, P. J. van der Put and J. Schoonman, *J. Physique C5*, 567 (1989).
5. Y. Kumashiro, *J. Mater. Res.* **5**, 2933 (1990).
6. C. C. Wang, M. Cardona and A. G. Fischer, *RCA Rev.* **25**, 159 (1964).
7. D. S. Ginley, R. J. Baughman and M. A. Butler, *J. Electrochem. Soc.* **130**, 1999 (1983).
8. A. Goossens, E. M. Kelder, R. J. M. Beeren, C. J. G. Bartels and J. Schoonman, *Ber. Bunsenges. Phys. Chem.* **95**, 503 (1991).
9. D. S. Ginley and M. A. Butler, *J. Electrochem. Soc.* **125**, 1968 (1978).
10. M. J. Madou, B. H. Loo, K. W. Frese and S. R. Morrison, *Surface Science* **108**, 135 (1981).
11. *Impedance Spectroscopy*, (Edited by J. Ross Macdonald) John Wiley & Sons Inc., New York 1987.
12. A. Goossens and J. Schoonman, *J. Electrochem. Soc.* **139**, 893 (1992).
13. A. Goossens and J. Schoonman, *J. Electroanal. Chem.* **289**, 11 (1990).