face portion low in dissolution rate and the interlayer more readily soluble into the developer may newly be exposed.

In a photosist subjected to partial development for 25 s, 80% thereof is dissolved and the NQD-ester deposits on the resist. The remaining 20% of the NQD-ester deposit can be reversibly hardened. Since triester is insoluble to the developer among the NQD-esters, it is very assumable that the NQD-ester layers partially rich in the triester exhibit a dissolution inhibition effect at the re-development. The foregoing mechanism is schematically shown in Fig. 14.

Another point to be discussed is the increment in the molecular weight upon light-exposure and development. Heating at the prebaking and the like induces azo-coupling between the novolak resin and the NQD. Since the compound resulting from this azo-coupling still comprises NQD groups, it undergoes decomposition upon light-exposure to form an intermolecular cross-linking. Accordingly, the increase in the molecular weight upon development is assumably closely related with the photolytic products, i.e., indeneketene and indenecarboxylic acid.

Conclusion

The development rate of a once partially developed photoresist residue depends on the duration of partial development. The dissolution rate is higher for those partially developed for shorter durations, but reversely, it signifies lower rate for those subjected to longer partial development, and eventually, the photoresist residue becomes insoluble in the developer during its re-development. In the case of light-exposed photoresist, the presence of NQD-esters was observed. It is therefore assumed that the NQD-esters, mainly the triester, deposits on the surface of the photoresist during the partial development, which thereby forms a dissolution inhibition layer.

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REFERENCES


An Impedance Study of Boron Phosphide Semiconductor Electrodes

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ABSTRACT

Impedance spectroscopy is employed in a study on the electrical and optical properties of boron phosphide (BP) electrolyte interfaces. With this technique both the space charge capacitance can be determined and the charge trapping in surface states can be investigated. The flatband potential of boron phosphide and the corresponding band-edge positions are found to be considerably more positive than the related III-V semiconductors GaP, GaAs, and InP. As a consequence, BP is found to be more stable for photo-etch reactions than any of these materials. It is shown that the band positions of GaP, GaAs, InP, and BP can be predicted from the atomic electronegativities fairly accurately. In neutral and alkaline electrolytes the surface of BP is free of native oxide and the surface state density is low. In acid electrolytes, however, a native oxide is present on the surface of BP. This oxide is probably hexagonal B2O3 and is observed to be able to cause a large shift of the bandedges. In the latter electrolytes the Mott-Schottky plots of BP are heavily distorted by the presence of additional surface state capacitances.

Electrochemical studies on GaP, GaAs, and InP, i.e., the III-V semiconductors, have provided detailed information on optical, electronic, and chemical properties of these materials. GaAs and InP possess an indirect bandgap of about 1.4 eV, and were investigated as electrode material in photovoltaic electrochemical (PEC) solar cells (1). These two materials are among the most efficient liquid junction light-to-electricity converting devices nowadays (2, 3). On the other hand, n-type GaP, GaAs, and InP are known to be photochemically unstable at electrode potentials which are positive with respect to their flatband potentials (4). The optically created holes at the semiconductor-electrolyte interface tend to oxidize the semiconductor rather than the electrolyte, leading to dissolution of the semiconductor. This phenomenon is conveniently used in photoelectrochemical photo-etching of III-V semiconductors, which is a promising technique for application in device technology.

Boron phosphide (BP) is the lightest III-V compound with semiconducting properties. Cubic BP crystallizes in the usual zinc-blende structure with a lattice parameter of 4.5383 Å (5). Its bandgap is indirect with an energy separation of 2.0 eV (5). The first direct transition is found at about 5.0 eV (6). Cubic boron phosphide is extremely inert chemically and resists all conventional etchants (7). Moreover, the Vickers hardness of BP resembles that of 7N which makes BP suitable as a ceramic hard coating material (8).

In this paper the electrochemistry of BP is discussed. Impedance spectroscopy is used to characterize this potential photoelectrode material with regard to its optical, electronic, and chemical behavior. Comparisons with the well known III-V semiconductors, i.e., GaP, GaAs, and InP shall be made frequently. In the first place, the flatband potential of monocrystalline cubic 100 n-type BP is derived accurately from Mott-Schottky plots. The presence of surface states at the BP/neutral or alkaline electrolyte interface is discussed. The surface state capacitance is analyzed to provide information on the density distribution of the surface states in energy space. At the BP/acid electrolyte interface, surface states are present, probably as the consequence of a native oxide on the surface of BP.
The presence of an oxide film in acid electrolytes also explains the large potential shift in the observed Mott-Schottky plots. Finally, the chemical stability of n-type BP for oxidation is discussed. It has been shown that photoholes at the BP/electrolyte interface give rise to surface recombination in optically created surface states, as could be observed by the occurrence of an additional capacitive contribution upon illumination. The optically created surface states are assumed to be a consequence of photoanodic dissolution of n-type BP. Such decomposition was observed indeed.

Experimental Aspects
At present, single-crystalline cubic boron phosphide is not available due to the impossibility of growing BP from the liquid phase. However, epitaxial cubic BP can be grown on crystalline silicon substrates by chemical vapor deposition (CVD) in a cold-wall reactor provided with radio-frequency heating. Using BPB1 and PBr3 liquid reactants, and H2 as carrier gas, epitaxial (100) BP layers could be grown on (100) Si wafers at 880 °C. The maximum growth rate obtained was about 1 μm/h. Details on the growth technique of BP were previously discussed (6). As a protonic contact, the Si/BP heterojunctions were sealed onto a PVC support and mounted into a three-electrode electrochemical cell made out of Teflon. A large-area Pt sheet, i.e., ~40 cm², served as counter electrode and a saturated calomel electrode (SCE) was employed as the potential reference. This reference electrode was shunted with a platinum wire, a so-called quasi-reference electrode, to prevent polarization of the SCE at high frequencies. Optical access to the Si/BP working electrode was possible through an optical-quartz window. It should be noted that we did not employ a rotating electrode in this study. A high-pressure xenon lamp (Oriel XBO 450 W) was used to generate electron/hole pairs in the photoelectrode. In the aqueous electrolytes, only nonactive ions were present. The electrolytes used were: H2SO4 (0.1 or 1 M), HCl (0.1 M), KCl (1 M) + NaAc (0.05 M) + HAc (0.05 M) + NaOH (0.1 M), and KOH (1 or 3 M).

The impedance of the cell was recorded with a Solartron impedance equipment. A Solartron Frequency Response Analyzer (FRA) Type 1250 was coupled to a Solartron Electrochemical Interface (ECU) Type 1286, which was used in its potentiostatic mode. Both instruments were controlled with a personal computer using IEEE interface communication. With this setup the impedance could be recorded as a function of the dc cell potential automatically.

The following instrument parameters were used. The generator stimulus amplitude was 10 mV. The dc bias was added to the ac stimulus by the potentiostat. An internal resistor in the electrochemical interface of 1000 Ω was used as a current-to-voltage converter. The bandwidth of the potentiostat was 1 MHz, which is an order of magnitude larger than the used frequency window of 0.8 Hz to 65 kHz. The measured ac signals were amplified by a factor of 10 before being transferred to the FRA.

The impedance data were fitted to an equivalent circuit using the nonlinear-least squares (NLLS) program "Equivalent Circuit" developed by Dr. B. A. Boukamp (6).

The observed parameter values of the circuit elements were plotted as a function of the cell potential from which the relevant data could be derived. It should be noted that the followed procedure yields circuit elements that are frequency independent.

Results
The equivalent circuit.—As was demonstrated in our previous paper (10), the Si/BP junction is very conductive with respect to the BP/electrolyte contact. In other words, the ohmic "short" at the Si/BP interface is negligible with respect to the "overpotential" at the BP/electrolyte interface at all practical current densities. Insamuch as the potential drop at the Si/BP junction is a few orders of magnitude smaller than the potential drop at the BP/electrolyte interface, it is disregarded.

At all occasions, the small-signal impedance of the electrochemical cell could be modeled using the equivalent circuit as presented in Fig. 1. The Q element in this circuit is characterized by an impedance \( Z_Q = K (\omega a)^{-s} \). If it approaches unity, \( Z_Q \) is identical to the impedance of an ideal capacitor. It should be noted that the circuit branches \( R_{BC}, R_{CB}, \) and \( R_{CB} \) were always significantly present. A circuit element is defined to be significantly present if the least squares residuals decrease by a factor of two or more for every additional free parameter.

The flatband potential.—The impedances of n-Si/n-BP, p-Si/n-BP, and n-BP with a shunted silicon substrate were recorded in the dark in all the different electrolytes mentioned above. The potential dependence of the \( K \) parameter of the \( Q \) element was evaluated. Since \( n \) is close to unity, i.e., 0.85 < \( n < 1 \), the \( K \) parameter may be regarded as nearly equivalent to a capacitance.

The graphs of \( K \) as a function of the cell potential \( V \) vs. SCE showed a smooth dependence in neutral or alkaline electrolytes and a peaked structure in acid electrolytes. Electrodes with a smooth \( K \) behavior will be denoted "clean," since, as will be pointed out, their surface is free of native oxide and has only low densities of trapping or recombination centers. The electrodes with peaked \( K \), i.e., BP electrodes in acid electrolytes, are termed "mottled," since a native oxide is present on the surface of BP and surface trapping or recombination is present on these electrodes to a large extent. Reliable values for the flatband potential can only be derived from impedance measurements on clean electrodes.

In buffered KCl, KOH, and NaOH the \( K \) plot was decreasing smoothly as a function of the cell potential in most cases. In these electrolytes the electrode surface was clean and the flatband potential could be derived from the linear relationship between \( K^2 \) vs. \( V \). According to the Mott-Schottky equation (11-13)

\[
C_v^2 = \frac{2e\varepsilon_0 n^*}{\varepsilon_r} \left( \Delta \varphi_{sc} - kT\varepsilon \right)
\]

where \( \Delta \varphi_{sc} \) denotes the potential drop across the space charge region. The potential drop in the electrode, \( \Delta \varphi_{sc} \), equals \( kT \varepsilon \) at the potential axis intercept, \( V_0 \), of the extrapolated plot of \( C_v^2 \) vs. \( V \), the so-called Mott-Schottky plot. Consequently, the flatband potential \( \varphi_{fb} \) is related to \( V_0 \) by \( \varphi_{fb} = V_0 - kT\varepsilon \). Since \( K^2 \) is linear in \( V \), the \( K \) parameter could be related to the space charge capacitance, \( C_v \). Apparently, the electrical field at the electrode surface is inhomogeneous, since a \( Q \) element describes the frequency dispersion more accurately than a pure capacitance. In Fig. 2 a Mott-Schottky plot of \( K^2 \) vs. \( V \) is presented. The extrapolated bias intercept reads 1.23 V vs. SCE in KOH electrolyte with a pH of 13.8 and was observed to depend on the pH according to a Nernstian ~60 mV/pH shift. As can be seen, the potential region where \( K^2 \) is linear in \( V \) exceeds half the 2.0 eV bandgap of BP. Since only n-type BP could be grown with our CVD technique, we were unable to confirm the flatband potential with p-type samples. It should be noted, however, that many different samples, obtained with different CVD parameters, exhibited the same flatband potential.

The energy difference between the conduction band of BP and the Fermi energy level in the bulk was determined by thermo-potential measurements. Without this potential drop, the thermoelectric voltage is termed "mottled," which refers to the Seebeck coefficient, i.e., d\( \varphi_{sc} \)/dT, which is related to \( \varphi_{fb} - \varphi_{tp} \) (14). For the BP electrodes \( \varphi_{tp} \), was about 50 mV at room temperature. The activation energy for
electrical conduction at room temperature was in good agreement with this value.

The point of zero charge (PZC) was determined with the method proposed by Ginley et al. (15). The point where the surface concentration of H⁺ equals that of OH⁻ is found at a pH of 6.4. The energy levels of BP are as follows

\[
E_e(BP) = (0.32 + 0.06 \cdot \text{pH}) \text{ eV vs. SCE}
\]

\[
E_v(BP) = (-1.68 + 0.06 \cdot \text{pH}) \text{ eV vs. SCE}
\]

Experimental accuracy = 0.05 eV

PZC(BP) is found at pH = 6.4

\[E_{	ext{SCe}}\] lies 4.75 eV below vacuum level.

BP electrodes with clean surfaces, from which the flatband potential was derived, had \( C_1 \) elements in the equivalent circuit which were often strongly dependent on the cell potential. Characteristic peaks in the \( C_i \) vs. V plots were frequently found and a typical example of \( C_1 \) vs. V with \( i = 1, 2, 3 \) is plotted in Fig. 3 (a), (b), and (c), respectively. In Fig. 3 (d) the potential dependence of the power factor \( n \) in the \( Q \) element is presented. With regard to the potential position of the dip in the \( n \) values a remarkable correspondence with the \( C_i \) peaks is present.

**BP electrodes with modified surfaces.**—Electrodes with modified surfaces are characterized by a peaked structure in the \( K \) vs. V graphs. A modified surface was present in \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \) electrolytes. Mott-Schottky plots of \( K^{-2} \) vs. V do not show a linear relationship over a reasonable potential region so that reliable values for the flatband potential could not be obtained from these plots. In Fig. 4 (a) a

---

**Fig. 2.** The potential dependence of the \( K \) value and the concomitant Mott-Schottky plot of \( K^{-2} \) vs. V of BP in concentrated KOH (3M).

**Fig. 3.** (a), (b), and (c) The potential dependence of the three parallel \( C_i \) capacitances \( (i = 1, 2, 3) \), and the potential dependence of power factor \( n \).
plot of $K$ vs. $V$ is presented for surface modified electrodes. The potential axis intercept, $V_m$ as derived from the extrapolation of the line connecting the observed two linear regions, is far more negative than $V_c$ at clean electrodes. The position of the peaks in the $K$ vs. $V$ graphs is very reproducibly present in acid electrolytes. The magnitude of the $K$ peaks, however, depends strongly on the history of the electrode and is not very reproducible. It was observed that cathodic charge flow in acidic electrolytes enhanced the peaks markedly.

_Illuminated BP electrodes._—Isotype n-Si/n-BP electrodes were irradiated with light of sufficient energy to create electron-hole pairs in BP, i.e., $E_{ph} > 2.0$ eV ($A < 620$ nm). At anodic biases and strong irradiation intensities photoholes reached the surface and were observed to oxidize $H_2O$ at the surface, leading to $O_2$ gas formation there. Stationary irradiated electrodes showed an additional peak in the $K$ vs. $V$ plots. This peak was observed to depend upon the irradiation intensity, but not in a linear way. When the light was switched off the peak disappeared restoring the initial $K$ and $C_i$ dependencies on the bias. In Fig. 5 a plot of $K$ vs. $V$ is shown.

**Discussion**

The positions of the energy bands of BP._—The positions of the conduction and valence bands of BP were derived from Mott-Schottky plots with respect to the reference SCE. In the following paragraphs, the experimental values for $E_C(BP)$ and $E_V(BP)$ shall be compared with the experimental band positions of other III-V semiconductors, i.e., GaP, GaAs, and InP. Moreover, it is shown to be instructive to compare the experimental $E_C$ and $E_V$ values of the III-V materials with the band positions derived from the semiempirical method using the atomic electronegativities (15).

The experimentally obtained band positions of III-V semiconductors may be compared with each other and

![Fig. 4. (a) The potential dependence of the $K$ parameter and (b) the concomitant Mott-Schottky plot of BP in acid electrolytes. (c) The superimposed distortion comprises two overlapping contributions presented by the curves in the overlap region.](image)

![Fig. 5. The influence of optical irradiation on the potential dependence of the $K$ parameter for BP electrodes in acid electrolytes.](image)
with the semiempirically calculated values only if the experimental data are corrected for additional potential drops in the Helmholtz layer due to specifically adsorbed H\textsuperscript{+} or OH\textsuperscript{-} species (15). If, however, the H\textsuperscript{+} and OH\textsuperscript{-} surface concentrations are equal, this potential drop is zero. The pH at which this occurs is the point of zero charge (PZC) and only at this pH the measured flatband potentials lead to band positions which can be regarded to be an intrinsic property of the III-V material. Hence, comparisons between the band positions of different semiconductor electrodes can be made only using data obtained at the pH of the PZC. However, since the PZCs of the III-V semiconductors are not exactly known, a value of pH = 7 is assumed as a reasonable approximation. The experimental band positions of GaP, GaAs, InP, and BP as derived from Mott-Schottky plots recorded in a pH = 7 electrolyte are compared.

In Table 1 and Fig. 6, it can be seen that both the conduction and valence bands of boron phosphide have low energy values. In particular, the valence band of BP lies very deep and is even found below the OFF /\textsubscript{2}O redox potential at 1.23 V vs. normal hydrogen electrode (NHE). The observed oxygen formation at illuminated n-type polycrystalline BP electrodes is in agreement with such a deep valence band energy position, as was pointed out in our previous paper (18).

The band positions of semiconductors can be estimated from a semiempirical method using the atomic electronegativities (19, 20). Mulliken’s definition of atomic electronegativity, \( \chi \), is used being \( \chi = 1/3 (I + EA) \) in which \( I \) is the atomic ionization energy and \( EA \) the electron affinity. The molecular electronegativity of a two-atomic molecule \( AB \) is given by \( \chi\text{mol}(AB) = \chi(A) \cdot \chi(B) / 2 \), which is related to the electrochemical potential of the electrons in a molecule being the Fermi-level position of the material. General semiconductor theory states that in intrinsic semiconductors, \( E_F \) lies nearly exactly in the center of the forbidden zone, i.e., \( E_F = (E_C + E_V) / 2 \). Hence, if both \( E_F \) and \( E_\text{g} \) (\( \approx E_C - E_V \)) are known, the band positions can easily be derived from \( E_C = E_F + 1/2 E_\text{g} \) and \( E_V = E_F - 1/2 E_\text{g} \).

In Table II the molecular electronegativities of the III-V semiconductors are presented. The values for \( I \) and \( EA \) were taken from Lange's Handbook (21).

In Table III, conduction and valence band positions are presented as calculated \( \chi\text{mol} \) values taken from Table II, together with the bandgap values from Ref. (5).

Table I. Experimental band energies vs. the normal hydrogen electrode (NHE) energy and the bandgaps of different III-V semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>( E_C ) (eV)</th>
<th>( E_C ) (NHE) (eV)</th>
<th>( E_V ) (NHE) (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>2.26</td>
<td>1.463</td>
<td>-0.737</td>
<td>(16)</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>1.318</td>
<td>-0.097</td>
<td>(16)</td>
</tr>
<tr>
<td>InP</td>
<td>1.35</td>
<td>0.832</td>
<td>-0.518</td>
<td>(17)</td>
</tr>
<tr>
<td>BP</td>
<td>2.0</td>
<td>0.484</td>
<td>-1.516</td>
<td>(10)</td>
</tr>
</tbody>
</table>

Table II. Molecular electronegativities as obtained from atomic values of \( I \) and \( EA \) for the III-V semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>( I ) (eV)</th>
<th>( EA ) (eV)</th>
<th>( 1/2(I + EA) ) (eV)</th>
<th>( \chi\text{mol} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>5.909</td>
<td>0.302</td>
<td>3.151</td>
<td>GaP = 4.208</td>
</tr>
<tr>
<td>P</td>
<td>10.406</td>
<td>0.743</td>
<td>5.615</td>
<td>GaAs = 4.089</td>
</tr>
<tr>
<td>As</td>
<td>9.81</td>
<td>0.805</td>
<td>5.308</td>
<td>InP = 4.134</td>
</tr>
<tr>
<td>In</td>
<td>5.786</td>
<td>0.302</td>
<td>3.044</td>
<td>B = 4.206</td>
</tr>
<tr>
<td>P</td>
<td>10.406</td>
<td>0.743</td>
<td>5.615</td>
<td>BP = 4.907</td>
</tr>
</tbody>
</table>

Table III. Calculated band positions using the molecular electronegativities and the bandgap energies.

<table>
<thead>
<tr>
<th>Material</th>
<th>( E_C ) (eV)</th>
<th>( E_V ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>2.26</td>
<td>5.326</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>4.799</td>
</tr>
<tr>
<td>InP</td>
<td>1.35</td>
<td>4.809</td>
</tr>
<tr>
<td>BP</td>
<td>2.0</td>
<td>5.907</td>
</tr>
</tbody>
</table>

In Table IV, the theoretically obtained conduction band positions are compared with the experimental values. The NHE energy position is taken 4.5 eV below vacuum level. As can be seen in Table IV, the relative deviation between semiempirically, \( E_F \) (th), and experimentally, \( E_F \) (exp), derived values is remarkably good.

Despite the simplicity of the approach, atomic ionization energies and electron affinities are found to provide a rather accurate quantitative description of the band positions of III-V semiconductors. Therefore, a discussion of these materials in terms of atomic properties seems to be justified.

Inasmuch as the ionization energy of boron \( I(B) \) is the only atomic property which strongly deviates from that of Ga and In (P and As having quite comparable ionization energies) this deviation is believed to be the origin of the differences found between the conduction and valence bands of BP and these bands for the other III-V materials. Using a common argument in molecular theories, the stabilization of the chemical bond in either molecules or crystals is enhanced by a large overlap between the atomic orbitals, as well as by a small energy difference between the constituent atomic orbitals. Since boron is the smallest main group III element, BP exhibits the smallest zinc-blende lattice parameter. In Table V the atomic radii of the main group III and V elements, \( r(\text{III}) \) and \( r(V) \), taken from Ref. (21), their sum, and the experimental nearest neighbor distance in the zinc-blende lattice, i.e., 0.433\( _a \), where a

Table IV. Comparison between calculated and experimental conduction band energies.

| Material | \( E_C \) (th) (eV) | \( E_C \) (exp) (eV) | \( \Delta E_C \) (eV) | \( \Delta E_C / E_C \) (\%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>3.079</td>
<td>3.037</td>
<td>+0.042</td>
<td>1.4</td>
</tr>
<tr>
<td>GaAs</td>
<td>3.379</td>
<td>3.187</td>
<td>+0.192</td>
<td>5.7</td>
</tr>
<tr>
<td>InP</td>
<td>3.459</td>
<td>3.636</td>
<td>-0.179</td>
<td>-5.0</td>
</tr>
<tr>
<td>BP</td>
<td>3.907</td>
<td>4.016</td>
<td>-0.109</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

Table V. The sum of the atomic radii of the constituent atoms compared with the nearest neighbor distance in the zinc-blende lattice.

<table>
<thead>
<tr>
<th>Material</th>
<th>( r(\text{III}) ) (( \AA ))</th>
<th>( r(V) ) (( \AA ))</th>
<th>( r(\text{III}) + r(V) ) (( \AA ))</th>
<th>0.433( _a ) (( \AA ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>1.25</td>
<td>1.10</td>
<td>2.35</td>
<td>2.360</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.25</td>
<td>1.21</td>
<td>2.46</td>
<td>2.448</td>
</tr>
<tr>
<td>InP</td>
<td>1.50</td>
<td>1.10</td>
<td>2.60</td>
<td>2.551</td>
</tr>
<tr>
<td>BP</td>
<td>0.88</td>
<td>1.10</td>
<td>1.98</td>
<td>1.968</td>
</tr>
</tbody>
</table>
equals the lattice parameter, are presented. From this table it can be derived that BP has the most compact crystal structure due to the small atomic radius of boron. Consequently, the overlap of atomic orbitals in BP exceeds the overlap in the other III-V semiconductors and stabilizes BP to a larger extent.

The second stabilizing factor is the small energy difference between the atomic orbitals which constitute the valence band of BP. This energy difference can be estimated from the atomic ionization energies. The difference between the ionization energies of molecule AB is defined as \( \Delta I = I(B)-I(A) \), and is presented in Table VI. From this table it can be read that \( \Delta I(BP) \) is much smaller than \( \Delta I \) for the other materials. Therefore, BP is stabilized most effectively by this comparatively small energy difference.

Both the overlap of atomic orbitals and the difference between the energy of the atomic orbitals, which are used to build the crystal wave functions, contribute to the stabilization of BP crystals more than in the case of the other III-V semiconductors. Moreover, both stabilizing effects can be thought of as originating from the small atomic radius of boron which leads to both a larger orbital overlap and a higher ionization energy. Of course the outlined discussion is not very rigid and primarily based on chemical intuition.

In the former section we discussed the Mott-Schottky behavior of the space charge capacitance and its consequences regarding the energy positions of the conduction and valence bands of BP. Now the behavior of parallel capacitances, \( C_B \), as a function of the potential will be discussed. As will be pointed out, these capacitances originate from charge trapping or recombination in surface states.

### Surface states in neutral or alkaline electrolytes

In neutral or alkaline electrolytes the parallel capacitances, \( C_i \), with \( i = 1, 2, 3 \) or 5, were found to exhibit a peaked structure which plotted as a function of the cell potential. Such a capacitance behavior is characteristic for charge trapping in surface states, as was explained in our previous paper on nonequilibrium surface recombination (22). The capacitance of surface charge trapping in monoelectronic surface states located at \( E_{BS} \) at semiconductor electrodes in equilibrium is given by

\[
C_{BS} = e^2N_a/4kT \cdot (\cosh(E_{BS} - E_F)/2kT)^{-2}
\]

where \( E_F \) denotes the Fermi level in an electrode which is in electronic equilibrium; the distribution of electrons for n-type or holes for p-type follows Fermi-Dirac statistics.

The maximum in the \( C_{BS} \) peak equals \( e^2N_a/4kT \) and the full width at half maximum (FWHM) can easily be derived from

\[
(\cosh(E_{BS} - E_F)/2kT)^{-1} = 1/2
\]

which directly leads to a FWHM value of 88.137 mV at room temperature; \( kT_e = 0.025 \) V. This FWHM value shall be denoted further the homogeneous line width (\( \Gamma_{hom} \)) following the usual spectroscopic notation.

The observed maxima of the \( C_i (i = 1, 2, 3) \) values, \( C_{max} \), in 3 molar KOH are presented in Table VII together with the potential for which these maxima are reached, \( V_{max} \), the FWHM, and \( \Gamma_{hom} \) being the inhomogeneous broadening factor. The inhomogeneous broadening is introduced since the observed capacitance peaks are usually much broader than 88 mV. As is further discussed, this can be explained by assuming a distribution of surface states within a certain energy region.

### Table VI. The energy differences between atomic ionization energies of the constituent atoms

<table>
<thead>
<tr>
<th>( \Delta I ) (eV)</th>
<th>GaP</th>
<th>GeAs</th>
<th>InP</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.487</td>
<td>3.811</td>
<td>4.700</td>
<td>2.188</td>
</tr>
</tbody>
</table>

Clearly inhomogeneous broadening occurs in all three parallel \( C_i \) vs. \( V \) curves. Such broadening can be ascribed either to a distribution of the applied potential difference, \( \Delta V \), over the Helmoltz layer, and the space charge layer, \( \Delta V = \Delta V_H + \Delta V_{SS} \), or to the presence of a distribution of surface states over a distinct energy interval. As shall be pointed out, the former possibility can be rejected.

The potential distribution over the Helmoltz and space charge layers can be calculated from the integral equation originally derived by Berglund (23) for MOS structures. If both the Helmoltz capacitance, \( C_H \), as well as the experimental total capacitance, \( C(V) = dQ_{total}/dV \), are known, then

\[ \Psi(V_2) - \Psi(V_1) = \int_{V_1}^{V_2} \left( 1 - \frac{C(V)}{C_H} \right) dV \]

where \( \Psi \) denotes the surface potential, and \( \Psi(V_2) - \Psi(V_1) = \Delta \Psi \).

Carrying out the numerical integration, using experimental \( C(V) \) values, leads to the conclusion that \( C_H \) must be made unrealistically small to be able to account for the observed line broadening. This can be easily confirmed by substitution of the average value of the experimental values of \( C(V) \) between \( V_1 \) and \( V_2 \), i.e. \( \langle C(V) \rangle = (V_2 - V_1)^{-1} \int_{V_1}^{V_2} C(V) dV \), into Eq. (2) and carrying out the integration analytically to yield

\[ \frac{\Psi(V_2) - \Psi(V_1)}{V_2 - V_1} = 1 - \frac{\langle C(V) \rangle}{C_H} \]

If a potential distribution accounts for the observed line broadening, the left-hand side of Eq. (3) equals the reciprocal of the inhomogeneous line broadening, \( C_{hom}/\Gamma_{hom} \), being about 0.2 in our case. Consequently, \( C_H = \langle C(V) \rangle \approx 0.8 \). Calculating \( \langle C(V) \rangle \) from the experimental data to be about 1 \( \mu F \) cm\(^{-2}\) leads to a value for \( C_H \) of 1.3 \( \mu F \) cm\(^{-2}\) which is at least an order of magnitude too small compared to the usually found \( C_H \) values of 20 to 50 \( \mu F \) cm\(^{-2}\).

The fact that an extremely small value of \( C_H \) is required to account for the observed line broadening leaves us to conclude that the observed inhomogeneous broadening in the \( C_i \) vs. \( V \) curves must be ascribed to a distribution of surface states over the potential span where \( C_i \) is found. The energy of the surface state may be distorted by small changes in the chemical environment on the surface; the surface being no longer homogeneous in composition. In order to derive the distribution function of the surface states from the observed capacitance peaks, a deconvolution must be carried out, as is schematically presented in Fig. 7. A Gaussian or Lorentzian distribution may be expected. As a consequence the surface state densities \( N_{ss} \) can no longer be derived from the maximum of the \( C_i \) vs. \( V \) peak, but must be the result of an integration over the peak. Estimating the order of magnitude of \( N_{ss} \) which now is an ensemble of monoelectronic surface states, yields \( N_{ss1} = 10^{14} \) cm\(^{-2}\), \( N_{ss2} = 10^{14} \) cm\(^{-2}\), and \( N_{ss3} = 3 \times 10^{14} \) cm\(^{-2}\).

The average energy position of the surface states is 0.23 eV below the conduction band edge for \( N_{ss1} \) and 0.28 eV below \( E_0 \) for \( N_{ss2} \) and \( N_{ss3} \).

DARK BP electrodes in acid electrolytes.—In acid electrolytes the K vs. V curves as presented in Fig. 4(a) are entirely different in shape than the ones recorded in alkaline electrolytes previously discussed. A peaked structure is observed within a certain potential region, whereas outside this region a smooth curve exists. If \( K \) is plotted vs.

### Table VII. The maxima of the \( C_i \) peaks, the concomitant potential, and the FWHM compared to the homogeneous line width.

<table>
<thead>
<tr>
<th>( C_i )</th>
<th>( V_{max} ) (V vs. SCE)</th>
<th>FWHM (V)</th>
<th>FWHM_{hom} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>20.5</td>
<td>-0.98</td>
<td>0.49</td>
</tr>
<tr>
<td>C2</td>
<td>21.8</td>
<td>-0.87</td>
<td>0.45</td>
</tr>
<tr>
<td>C3</td>
<td>7.2</td>
<td>-0.87</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Fig. 7. Schematic illustration of an inhomogeneously broadened surface state capacitance peak.

As presented in Fig. 4(b), two linear regions lying on a single line are found with a distorted region in between. This K vs. V behavior indicates two additive contributions to the K value. K must contain both the space charge capacitance and superimposed a second capacitive component due to charge trapping in surface states. Hence, the circuit element $Q_{SS}$ in Fig. 1 must be further differentiated into $Q_{SC}$ and $Q_{SS}$, as presented in Fig. 8.

The elements $Q_{SC}$ and $Q_{SS}$ can be observed as a single Q if both $R_n$ is small and the two powers of n are equal. If this is the case $K_T$ can be obtained from the two linear regions in the $K^{-2}$ vs. V graph and the Mott-Schottky plot can be constructed as is shown in Fig. 4(b). The potential axis intercept of the $(K^2)^{-1}$ vs. V plot, $V_n$ equals $-1.5$ V vs. SCE and from the slope a donor density $N_D$ of $1.28 \times 10^{16}$ cm$^{-3}$ can be derived. Subsequently the $K_{SS}$ values can be subtracted from the experimental K values using a linear interpolation in the distorted region of the Mott-Schottky plot to find the remaining $K_{SS}$ component. In the Fig. 4(a) and (b) this interpolation is presented as a dashed curve. In Fig. 4(c) the residual $K_{SS}$ contribution is presented. As is shown in this figure, the $K_{SS}$ vs. V curve contains two overlapping peaks. The lines represent the two individual peaks in the overlap region. Apparently, two surface states are present which contribute additively to the observed $K_{SS}$. The parameters derived for these two contributions are presented in Table VIII.

The Mott-Schottky plot of the $K_{SS}$ component has a potential axis intercept, $V_0$, which lies about 1.3 V negative to the position where the flat band potential would be in the undisturbed case as can be derived from the $K_{SS}$ behavior in neutral or alkaline solutions. This can be understood as follows. If $C_{SS}$ and $C_H$ are of about the same magnitude, the applied potential is distributed across the space charge and Heimholtz regions. For that case De Gryse et al. (24) derived an expression for the total capacitance. Their findings result in a negative shift of the potential axis intercept, $V_0$, when the slope of the Mott-Schottky plot remains unaltered. The potential axis intercept for this case is given by

$$V_0 = V_{FB} + kT e / 4 \pi \varepsilon_0 N_D / 2 C_H^2$$

[6]

The cathodic shift is given by $4 \pi \varepsilon_0 N_D / 2 C_H$, which equals 1.3 V in our case. Using $N_D = 1.28 \times 10^{16}$ cm$^{-3}$, as derived from the Mott-Schottky slope, a value of $9.8 \mu$F cm$^{-2}$ is found for $C_H$ which is a rather small but acceptable value for the Heimholtz capacitance.

This $C_H$ value can be used to explain the inhomogeneous broadening of the $K_n$ peaks. As was previously discussed, $\Delta \psi / \Delta V$ can be estimated from Eq. [5]. Calculating a value of $4 \mu$F cm$^{-2}$ for the experimental mean capacitance, $<\psi(V)>, \Delta \psi / \Delta V = 1 - 0.4 = 0.6$, which results in a FWHM $\Delta \psi_{hom} = 1.7$. This is in fair agreement with the experimental values. Consequently, nearly monoenergetic surface states are present at $-0.35$ and $0.12$ V vs. SCE. The surface state densities are found to be $2.2 \times 10^{12}$ and $5 \times 10^{11}$ cm$^{-2}$, respectively. The positions of the surface states in the bandgap can be derived with the use of Eq. [6] and are 0.68 and 0.06 eV below the conduction band, respectively.

When we used De Gryse's formula to calculate the value for $C_H$, additional potential drops due to the surface states charges were disregarded. The justification of this is given by the fact that the two linear regions in the $K^{-2}$ vs. V plot lie on a single line. Moreover, using a value about $10 \mu$F cm$^{-2}$ and the given surface states densities, the total potential shift due to these additional surface charges is found to be less than 50 mV.

The rather small Heimholtz capacitance of about $10 \mu$F cm$^{-2}$ may be the result of an oxide film on the electrode surface. SEM and X-ray analyses indeed confirmed the existence of a native oxide on BP in acid electrolytes. This native oxide was characterized by X-ray diffraction to be hexagonal $B_2O_3$. In SEM micrographs this film looks quite compact and isotropical on the surface.

**Illuminated BP electrodes in acid electrolytes.** When n-type BP electrodes in an acid electrolyte are irradiated, electron-hole pairs are created. If depletion exists, the electrons drift into the bulk of the solid, whereas the holes drift towards the surface to drive an oxidation reaction there. In the III-V semiconductors, GaP, GaAs, and InP, it is generally accepted that the semiconductor itself is oxidized by photoholes rather than electroactive species in the electrolyte. This phenomenon has been observed by many different techniques (4, 23-28). One of the most sensitive of these is the observation of a surface state capacitance that is a function of the irradiation intensity. Capacitance peaks can show up when the light is switched on, and disappear again when the light is switched off. As was pointed out in our previous paper (23), the optically induced capacitance peaks are usually accurately described by the equilibrium expression, i.e., Eq. [2].

As shown in Fig. 5 optically reduced capacitance peaks appear at n-type BP electrodes. The capacitance peak already present at $-0.35$ V vs. SCE increases when the light intensity increases. Moreover, an additional peak, absent in the dark, appears at 0.55 V vs. SCE as a result of bandgap irradiation. As was pointed out by Matsumoto et al. (25) such capacitance effects must be ascribed to the onset of oxidation of the electrode due to the presence of photoholes at the semiconductor/electrolyte interface. In our case, the principal chemical reaction may then be written as $BP + 6H_2O \rightarrow BP^* + P + 6H_2O$. Hence, a multistep reaction mechanism is involved, and if one of the reaction intermediates introduces an electronic level within the forbidden zone this gives rise to surface recombination and a concomitant surface state capacitance. Consequently, BP, similar to the other III-V semiconductors, is oxidized by photoholes at the surface. Since, however, unlike the other III-V semiconductors, oxygen formation is observed at irradiated n-type BP electrodes, a competition between the oxidation of the solid and of OH$^-$ species occurs reflecting the lower valence band position of BP and the concomitant larger stability of BP against photonoic oxidation.

![Table VIII. The maxima of the $K_n$ peaks, in acid electrolytes, their potentials, and the FWHMs compared to the homogeneous line widths.](image)
Conclusions

Impedance spectroscopy can be used to obtain accurate values for the conduction and valence band positions of BP in neutral or alkaline electrolytes. In these electrolytes the energies found are in line with the band positions of the other III-V semiconductors, GaP, GaAs, and InP. A simple semiempirical model based on the atomic electronegativities yields band energy positions which agree with the experimental data to a surprising accuracy. The low lying conduction and valence bands of BP can be thought of as a consequence of the small atomic radius of boron.

In alkaline, neutral, and acidic electrolytes, surface states on BP are present. In alkaline and neutral electrolytes, these surface states have a broad energy distribution, whereas this distribution is small in an acidic electrolyte. Moreover, an oxide layer of probably B2O3 is present in acidic electrolytes and probably accounts for the observed potential distribution over the Helmholtz and space charge layers.

Holes present at the BP/electrolyte interface are involved in two competing processes, namely, the oxidation of the semiconductor and the oxidation of the OH” species. In order to define the ratio between these charge transfer processes and to elucidate the actual reaction mechanism involved in the photooxidation of BP, more experiments are required. Impedance spectroscopy can play an important role in unraveling this mechanism.

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