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DEPOSITION OF CUBIC BORON MONOPHOSPHIDE FROM BBr_3 AND PBr_3 : A REACTION MECHANISM

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Abstract -The CVD growth kinetics of polycrystalline cubic BP at atmospheric pressure were studied for the BBr_3-PBr_3-H_2 system using in situ thermogravimetry. In the temperature range 1050-1350 K the deposition obeys Langmuir-Hinshelwood kinetics having two different activation enthalpies. These are consistent with different rate limiting reactions in two temperature regimes. At low temperature PBr_3 is the main adsorbed species and the activation enthalpy is 224 kJ/mole due to substrate-phosphorus bond breaking of chemisorbed phosphorus species. At higher temperatures when the main adsorbed species is P_2 the reaction is determined by an activation enthalpy of 247 kJ/mole due to P=P bond breaking of the P_2 species at the surface. The order in H_2 decreases with temperature from 1/2 at low temperature to zero at high temperature. The effect of the gas phase hydrogen partial pressure on the growth kinetics is explained by a higher affinity of H_2 towards the substrate-phosphorus bond than towards the P=P bond of adsorbed P_2.

1.-Introduction.

The synthesis and characterization of two crystalline boron phosphides have been reported, i.e. cubic boron monophosphide BP /1/, and a rhombohedral boron subphosphide B_6P or $B_{13}P_2$ /2/. Amorphous boron phosphides have been described as boron rich boron phosphide a-B_xP, with x ranging from 3 to 13 /3,4/.
BP is a III-V semiconductor having an indirect bandgap of 2 eV /5/. BP is very hard and resistant to chemical corrosion /6/. It dissolves under hydrothermal conditions in concentrated nitric acid and alkali hydroxide. It oxidizes in air above 800 °C with formation of BPO_4 /1/. Therefore, cubic BP is an interesting compound for thin film applications.
BP dissociates into a lower phosphide B_6P and gaseous phosphorus if heated above 700 °C. This dissociation precludes synthesis of BP directly from the elements since the melting point of boron is over 2000 °C. In order to develop thin films of BP Chemical Vapor Deposition (CVD) is used in a reducing hydrogen atmosphere with bromide reactants. The reaction mechanism has been shown previously to obey Langmuir-Hinshelwood kinetics /4,7/. At about 925°C a transition has been observed in the growth kinetics, which has previously been shown to result from a change in adsorbed phosphorus containing species, i.e. from PBr_3 to P_2. This change was also confirmed by thermodynamic calculations. However, the calculated energies observed from a least squares fit, remain to be explained in terms of the observed Langmuir-Hinshelwood reaction mechanism. This assessed reaction mechanism is discussed briefly. Here we shall report on the assignments of the energies involving chemical bonds between species. Finally we shall discuss the role of the carrier gas hydrogen on the reaction growth rate, below and above the transition temperature.

2.-Experimental aspects.

A thermobalance CVD set-up equipped with a vertical hot-wall fused-silica tube reactor (ID 26 mm) as described previously /4,7/ is used to determine growth rates of polycrystalline cubic BP as a function of temperature, BBr_3, PBr_3, and H_2 reactant gas partial pressures at atmospheric pressure. Mixtures of helium and hydrogen are used as carrier gases. Substrates were alumina chips cleaned as described previously /4,7/.

3.-Results and discussion.

An experimental CVD diagram of the solid phases as reported earlier /7/ is shown in Figure 1. Here we shall limit the discussion to the regime of cubic BP formation.

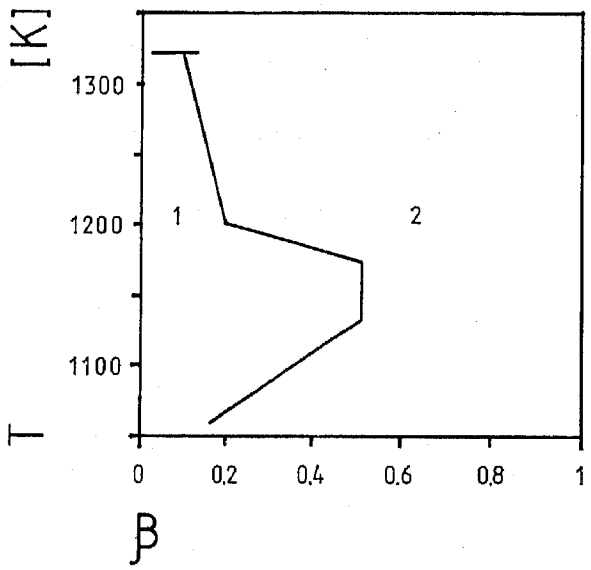

Fig. 1. Process conditions for deposition of polycrystalline cubic boron monophosphide BP (1), and amorphous boron phosphide BxP (2), with x ranging from 3 to 13 and $\beta = p(BBr_3)/(p(BBr_3)+p(PBr_3))$.

Growth rate measurements were performed by changing input partial pressures and temperature. We observed for the growth rate at low BBr_3 input pressure a linear increase with BBr_3 vapor pressure. Deviation from linearity occurs at higher reactant partial pressures (Fig. 2). For PBr_3 we find at zero input partial pressure boron formation, at low input amorphous BxP formation, and above certain input partial pressures a steep increase in the BP growth rate, which decreases exponentially at still higher input. The order in the PBr_3 for high input changes above 925 °C from -1 to $-\frac{1}{2}$ (Fig. 3).

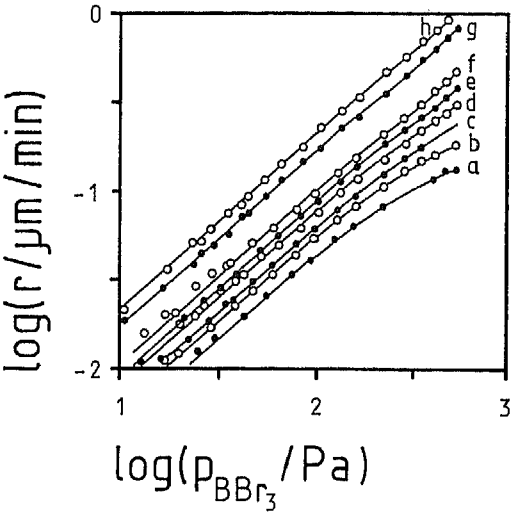

Fig. 2. Logarithmic plot of the growth rate r versus BBr_3 pressure for several temperatures (°C) at constant PBr_3 pressure (405 Pa). a: 800; b: 821; c: 840 d: 860; e: 880; f: 902; g: 931; h: 962.

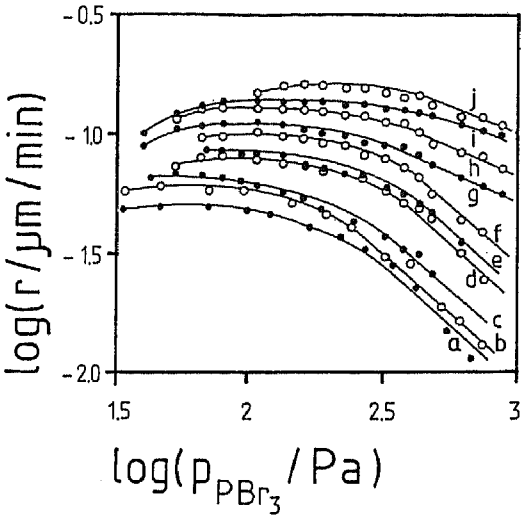

Fig. 3. Logarithmic plot of the growth rate r versus PBr_3 pressure for several temperatures (°C) at constant BBr_3 pressure (45 Pa). a: 800; b: 821 c: 840 d: 860; e: 881; f: 904; g: 906; h: 967 i: 1008; j: 1058.

This change in reaction order can be understood by assuming Langmuir-Hinshelwood adsorption behavior /8,9/ for different gas species which compete for the same adsorption sites. The temperature dependence of the growth rate is different at temperatures below and above 925 °C. According to thermodynamic equilibrium calculations, at low temperatures, the competitive species are BBr /10/ and PBr_3, whereas at high temperature the competitive species are BBr /10/ and P_2. P_2 is assumed to adsorb dissociatively, requiring 2 adjacent sites simultaneously, and leading to a reaction order of -1/2 for high input /8,9/. Actually PBr_3 is detected at low temperatures at the outlet of the reactor, whereas at higher temperatures it is not detected. At low temperatures where P_4 is thermodynamically in excess /7/ compared to P_2 the reactive species is PBr_3, whereas at high temperature where P_2 is thermodynamically in excess compared to P_4, and no PBr_3 is available, the reactive species is P_2. P_4 is not involved in the reaction according to our model. The growth rates for both mechanisms are:

$$r_1 = \frac{k_{r1} K_B P_B K_P P_P}{(1+K_B P_B + K_P P_P)^2} \qquad (1)$$

$$r_2 = \frac{k_{r2} K_B P_B (K_{P2} P_{P2})^{1/2}}{(1+K_B P_B + (K_{P2} P_{P2})^{1/2})^2} \qquad (2)$$

r_1, r_2 : growth rate at $T < 925$ °C, and $T > 925$°C, respectively.
k_{r1}, k_{r2} : reaction rate constant for reaction r_1 and r_2, respectively.
K_B, K_P, K_{P2} : heat of adsorption for species BBr, PBr_3, and P_2, respectively.
P_B, P_P, P_{P2} : partial pressure of species BBr_3, PBr_3, and P_2, respectively.
Note that P_{P2} equals the PBr_3 input partial pressure due to complete conversion of PBr_3 to P_2.

A least squares fit to the measured kinetics yielded the following values for the Langmuir-Hinshelwood parameters.

$k_{r1} = \exp[-27000/T+24.72]$ $E_{a1} = 224$ kJ/mole (3)
$k_{r2} = \exp[-29700/T+27.15]$ $E_{a2} = 247$ kJ/mole (4)
$K_B = \exp[24500/T-27.44]$ $\Delta H_B = 204$ kJ/mole (5)
$K_P = \exp[10700/T-13.52]$ $\Delta H_P = 89$ kJ/mole (6)
$K_{P2} = \exp[23000/T-22.20]$ $\Delta H_{P2} = 191$ kJ/mole (7)

E_{a1}, E_{a2} : reaction activation enthalpy for reaction r1 and r2, respectively.
ΔH_B, ΔH_P, ΔH_{P2} : heat of adsorption for BBr, PBr_3, and P_2, respectively.

These energies, i.e. (3)-(7) remain to be explained in terms of the observed Langmuir-Hinshelwood reaction mechanism. The calculated energies from the Langmuir-Hinshelwood reaction mechanism shall be assigned involving chemical bonds between species. In Table 1 several binding energies are listed which will be shown to be important in the assumed Langmuir-Hinselwood kinetics. A tentative model is given below.

Table 1. Binding energies of boron, phosphorus, and hydrogen /11/.

Bond	Energy / kJ/mole	From:
B - B	190 - 230	Boron sublimation; $B_{(s)} \longrightarrow B_{(g)}$
P - P	210 - 230	Phosphorus (black) sublimation; $P_{(s)} \longrightarrow P_{(g)}$
P = P	488 - 496 [1)]	Diphosphorus dissociation; $P_{2(g)} \longrightarrow 2\ P_{(g)}$
B - P	200 - 250	$BP_{(s)}$ dissociation; $BP_{(s)} \longrightarrow B_{(g)} + P_{(g)}$
B - P	10 - 100	$X_3B\text{-}PY_{3(g)} \longrightarrow BX_{3(g)}+PY_{3(g)}$; dissociation /12/
H - H	435 - 447 [1)]	Hydrogen dissociation; $H_{2(g)} \longrightarrow 2\ H_{(g)}$

[1)] Note that the binding energy in the Langmuir-Hinshelwood reaction mechanism should be taken per mole P or H. The dissociation energy however is given in kJ/mole P_2 or H_2.

The reaction mechanism below 925°C. The value of ΔH_B, i.e. 204 kJ/mole (Eq. (5)) corresponds to the heat of adsorption of BBr on BP. This heat of adsorption seem to be in line with the binding energy of B-P or B-B (Table 1). Hence, the heat of adsorption of BBr can be assigned to B-P or B-B bond formation. Similarly the value of ΔH_P, i.e. 89 kJ/mole (Eq. (6)), which seems to lie between that of a physisorption and a chemisorption process, corresponds to the heat of adsorption of PBr_3 on BP. This heat of adsorption is similar to the binding energy of B-P found in adducts $X_3B\text{-}PY_3$ (Table 1), where X and Y represent either halogen or hydrogen. Hence, the heat of adsorption ΔH_P can be assigned to B-P bond formation with binding energy as observed in $X_3B\text{-}PY_3$. The reaction activation enthalpy E_{a1}, i.e. 224 kJ/mole (Eq. (3)), is similar to the binding energy of P-P (Table 1). Hence, the reaction activation enthalpy is necessary to break a P-P bond. This P-P bond breaking is tentatively assigned to a desorption of a chemisorbed phosphorus species from the surface. Using the results of equations (3), (4), and (6) it is possible to calculate the phosphorus surface concentration /8/. The calculations reveal the surface seems to be covered almost completely by phosphorus. Thus it is not surprising to find that the reaction rate is controlled by a desorption process involving phosphorus. Consequently this desorption leaves a free adsorption site on which BBr or PBr_3 can adsorb. The adsorbed BBr species takes care of the progression of the reaction. The model is shown in the reactions (8)-(13). Gaseous species are unlabeled, * represents a free adsorption site, the label * indicates an adspecies, and <BP> represents solid cubic boron monophosphide. Reactions (9) and (12) are written as overall reaction steps since we cannot assign how H_2 is involved in separate reaction steps. Neither is it possible to calculate an activation enthalpy of reactions (9) and (12). However, the activation enthalpies of

reactions (9) and (12) are certainly much lower than the observed activation enthalpy of reaction (10) since this was the rate controlling step. Although the nature of the adspecies B* and P* is unknown, they are assumed to be monoatomic. The nature of the phosphorus adspecies will be discussed later.

$$PBr_3 + * \rightleftharpoons PBr_3^* \qquad \Delta H_P = 89 \text{ kJ/mole} \qquad (8)$$

$$PBr_3^* + 1\tfrac{1}{2}\, H_2 \longrightarrow P^* + 3\, HBr \qquad (9)$$

$$P^* \longrightarrow P + * \qquad E_{a1} = 224 \text{ kJ/mole} \qquad (10)$$

$$BBr + * \rightleftharpoons BBr^* \qquad \Delta H_B = 204 \text{ kJ/mole} \qquad (11)$$

$$BBr^* + \tfrac{1}{2}\, H_2 \rightleftharpoons B^* + HBr \qquad (12)$$

$$P^* + B^* \longrightarrow \langle BP \rangle + 2\, * \qquad (13)$$

The reaction mechanism above 925 °C. The ΔH_B value observed by the least squares fit of equation (1) is taken to be the same for equation (2). This assumption can be justified by a complete fit of equation (2), where we found ΔH_B being the same within the error of the measurements. The ΔH_{P2} value, i.e. 191 kJ/mole (Eq. (7)) corresponds to the heat of adsorption of P_2. This heat of adsorption equals almost twice the heat of adsorption of PBr_3 found for low temperature depositions. Thus, per mole P the heat of adsorption of P_2 equals almost the heat of adsorption of PBr_3. In the assumed Langmuir-Hinshelwood reaction mechanism (Eq. (2)) dissociation should occur. The dissociation of P_2 in the gas phase needs 488-496 kJ/mole P_2 (Table 1). According to catalysis the dissociation energy of P_2 is assumed to be the same at the surface. The dissociation energy of P_2, i.e. 488-496 kJ/mole P_2, is equal to 244-248 kJ/mole P formed upon dissociation. This value is in line with the observed activation enthalpy of equation (2), i.e. 247 kJ/mole. Hence, the dissociation of P_2 on the surface seems to be the rate limiting step at high temperatures. The monoatomic phosphorus formed in this dissociation process is assumed to be physisorbed. We already know from the low temperature kinetic measurements that the desorption energy of chemisorbed phosphorus is 224 kJ/mole P (Eq. (10)). Neglecting a probably small adsorption activation enthalpy, the adsorption energy equals the desorption energy by changing sign. Therefore, the chemisorbed phosphorus species P*-level has already been determined (Fig. 4), i.e. two times 224 kJ/mole P below the 2P+2*-level. The energy difference ΔH_{Pc} between physisorbed and chemisorbed phosphorus, P^x and P*, respectively, becomes therefore (2*224-191)/2=129 kJ/mole P. The activation enthalpy to free an occupied surface site from phosphorus, i.e. 224 kJ/mole will be less important relative to the observed activation enthalpy, i.e. 247 kJ/mole. The reaction mechanism can be written by reaction steps (11)-(13) and the following reactions:

$$2\, PBr_3 + 3\, H_2 \longrightarrow P_2 + 6\, HBr \qquad (14)$$

$$P_2 + xx \rightleftharpoons P_2^{xx} \qquad \Delta H_{P2} = 191 \text{ kJ/mole } P_2 \qquad (15)$$

$$P_2^{xx} \longrightarrow 2\, P^x \qquad E_{a2} = 247 \text{ kJ/mole} \qquad (16)$$

$$P^x + * \longrightarrow P^* + x \qquad \Delta H_{Pc} = 129 \text{ kJ/mole P} \qquad (17)$$

$$P^* \longrightarrow P + * \qquad E_{a1} = 224 \text{ kJ/mole} \qquad (18)$$

The symbols are the same as described for reactions (8)-(13), x represents a free physisorption site, and the label x indicates a physisorbed adspecies. In Figure 4 both models are summarized in an energy versus reaction path plot. The value ΔH_{Pc} is also used for the energy difference of adsorbed PBr_3 to chemisorbed phosphorus P*.

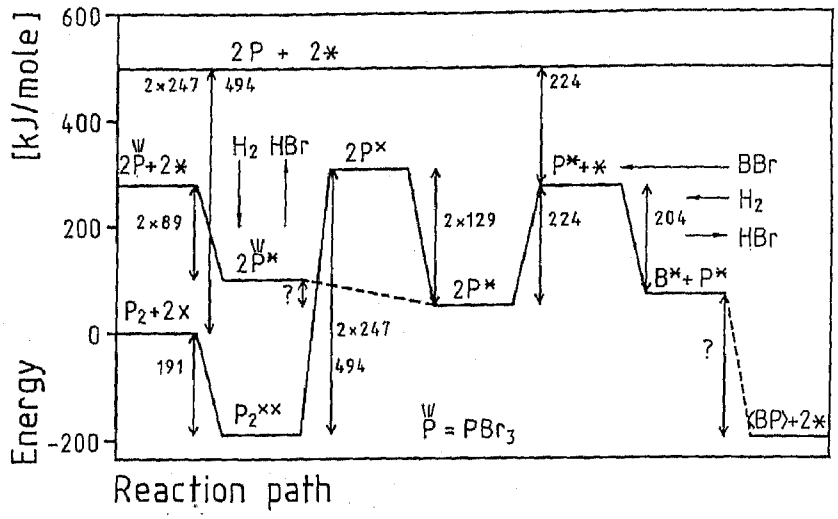

Fig. 4. Reaction path scheme with heats of adsorption for the corresponding species and activation enthalpies for both reaction mechanisms. Symbols as mentioned in the text.

The model of dissociation after physisorption is discussed in Ref. 9. The chemisorbed phosphorus atoms P* show up an endothermic adsorption relative to P_2. The existence of endothermic adsorption was already observed and discussed by de Boer /13/ and Thomas /14/. The model was extensively discussed along with dissociative adsorption of H_2 on several different substrates, with initially physisorption of H_2. De Boer /13/ and Thomas /14/ explained the existence of endothermic adsorption by the change of entropy on adsorption. Thomas /14/ concluded that only endothermic chemisorption is possible.
Experimentally, the dissociation of BP into BxP and P_2 can be understood by this reaction scheme (Fig. 4), due to the low lying level of physisorbed P_2. We also can understand the formation of only n-type semiconducting BP /7/ by incorporation of phosphorus, which is available in excess at the surface. This excess phosphorus precludes p-type semiconducting BP formation. However, if several free surface sites become available for BBr adsorption, i.e. on going to higher temperatures or lower PBr_3 input partial pressure, BxP will be formed (Fig. 1) due to the high activation enthalpy of P_2 dissociation. Hence, BxP formation will be formed though there is an excess of phosphorus available as P_2.

We have also obtained the growth rates of polycrystalline BP as a function of the hydrogen partial pressure. From Figure 5 which shows the results, it follows that at temperatures below 925 °C the reaction order in H_2 is $^1/_2$ whereas at temperatures above 925 °C this order shifts to zero.
The order $^1/_2$ shows up if equation (12) would be limiting the growth rate. However, this reaction cannot account for an order -1 and $-^1/_2$ for the PBr_3 reactant. Hence, equation (12) will not be rate limiting. The observed transition in reaction order in the phosphorus reactant on going to higher temperatures concomitant with a change in reaction order in hydrogen , can be understood from the behavior of the main phosphorus species P* present on the surface. In the outline of the reaction mechanism given above, this species was unspecified. The observed order in H_2 suggests that P* probably is covalently bound PH_2*.

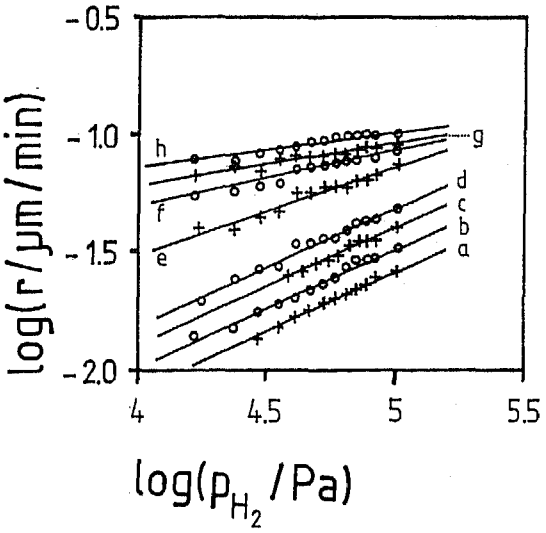

Fig. 5. Logarithmic plot of the growth rate r versus H_2 pressure for several temperatures (°C) at constant BBr_3 and PBr_3 pressure of 45 and 405 Pa respectively. a: 828; b: 852; c: 878; d:902; e: 928; f: 952; g: 977; h: 1004.

We calculated the surface concentration by assuming a change in enthalpy and entropy of the gas species on adsorption. The enthalpy change is taken to be the observed bond energy as calculated by the least squares fit. The entropy change is calculated by the loss of translation and rotation entropy of the gas species and the gain of vibration entropy of the adspecies. The complete model and the results will be published elsewhere.
The most striking result of the calculations is the almost complete coverage of the surface by PH_2 adspecies bound to boron atoms as well as to phosphorus atoms already incorporated in the substrate. Desorption of excess PH_2*, necessary to free an occupied surface site, is controlled by a gas phase reaction of PH_2 with H_2 to form PH_3 according to equation (20). Equation (20) is given as an overall reaction since it is not known how H_2 reacts in separate steps. PH_3 is calculated to be present in the gas phase in considerable quantities /7/.

$$PH_2^* \rightleftarrows PH_2 + * \qquad (19)$$

$$PH_2 + \tfrac{1}{2}\,H_2 \longrightarrow PH_3 \qquad (20)$$

The P-P bond breaking needed for desorption of excessively present PH_2 and hence for the progression of the reaction is consistent with the reaction activation enthalpy of 224 kJ/mole. However, the reaction can also occur by initial adsorption of the PH_3 species formed by the reaction with H_2 (see equation (21)). Here too, the role of H_2 is not known in separate steps.

$$PH_2^* + \tfrac{1}{2}\,H_2 \rightleftarrows PH_2^* \longrightarrow PH_3 + * \qquad (21)$$

The desorption activation enthalpy, however, will have the same order of magnitude as the heat of adsorption of PBr_3, i.e. 89 kJ/mole. This means that this P-P bond breaking cannot explain the reaction activation enthalpy. However, Table 1 shows that the dissociation energy of H_2 is 435-447 kJ/mole H_2, or 217-224 kJ/mole H. The dissociation energy, i.e. 217-224 kJ/mole H is in good agreement with the observed activation enthalpy at low temperature (Eq. (3)).Hence in the event of initial adsorption of PH_3 formed by the reaction of adsorbed PH_2 with gaseous H_2 the reaction is controlled by dissociation of H_2.

The decrease of the reaction order towards higher temperatures can be understood by the nature of the reaction. In this temperature range the reaction activation enthalpy increases to 247 kJ/mole presumably due to P≡P bond breaking. This high activation enthalpy will mask the lower activation enthalpy of 224 kJ/mole, resulting in a reaction rate which will become independent on the hydrogen partial pressure under study. Both models described above predict a zero order in hydrogen towards higher temperatures. Hence, to discriminate between these alternative mechanisms, growth rates must be measured as a function of BBr_3, and PBr_3 partial pressure and temperature at several different H_2 partial pressures.

4.- Conclusions.

Polycrystalline cubic BP can be synthesized by Chemical Vapor Deposition of BBr_3, PBr_3 in a reducing atmosphere of hydrogen. The regime of BP formation determined by temperature and molar ratios of reactants, however, is narrow. In the temperature range between 1050 and 1350 K the deposition rate obeys Langmuir-Hinshelwood kinetics. At low temperatures PBr_3 is the main adsorbed species competing for the same adsorption sites with BBr. The activation enthalpy, i.e. 224 kJ/mole, is due to surface-phosphorus bond breaking of chemisorbed phosphorus species. At higher temperatures when the main adsorbed species is P_2, which adsorbs dissociatively and competes for the surface sites with BBr, the reaction is determined by an activation enthalpy of 247 kJ/mole due to P=P bond breaking.
A change of the order in PBr_3 at high input from -1 to $-\frac{1}{2}$ towards higher temperatures is accompanied by a change of the order in hydrogen from $\frac{1}{2}$ to zero. The surface phosphorus species is probably PH_2 which will desorb on reaction with H_2 resulting in an activation enthalpy of 224 kJ/mole due to P-P bond breaking and an order in H_2 of $\frac{1}{2}$. The activation enthalpy of 224 kJ/mole can also be explained by dissociation of H_2 to form PH_3 which will desorb with an activation enthalpy of the order of magnitude of the heat of adsorption of PBr_3, i.e. 89 kJ/mole.
At temperatures above 925 °C the reaction become independent of the H_2 partial pressure since H_2 is not involved in the rate limiting step, i.e. P=P bond breaking. Hence, the order in H_2 becomes zero on going to higher temperatures.

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