DEPOSITION PROCESSES OF BORON AND BORON NITRIDE BY PLASMA JET IN RAREFIED GAS.

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ABSTRACT

By injecting Boron trichloride in argon or nitrogen rarefied plasma, we obtained after dissociation and condensation on substrate, thin layers of boron or boron nitride. The quick growing of deposit is in good agreement with theoretical calculations.

1. INTRODUCTION

Our deposition processes for obtaining coating of boron an boron nitride are founded on the following principle : gaseous boron trichloride is introduced into the plasma of argon or nitrogen, where it is dissociated. So we synthetize on a substrate, refractory film by condensation. (1), (2), (3). In this paper we quickly describe the experiments and the experimental results : boron and boron nitride amorphous have been obtained with a good efficiency and a short deposition time.
A theoretical study has been worked out and is compared with experimental results.

2. APPARATUS.

The wind tunnel allows of a large size container in steel in which three pumps maintain a pressure of 0.1 torr with a gas flow of 8000 m^3/h. The limit pressure is ranging about 10^{-3} torr. The plasma torch is composed of a copper blast-pipe which is the anode and the cathode is in tungsten alloyed with 2 % thorium. A direct current rotative generator provides the arc (with argon : 20 V, 200 A ; with nitrogen : 40 V, 200 A). (4) (5). An electromagnetic coil, surrounding the blast-pipe, allows the rotation of arc and prevents thus the destruction of the anode. The whole is water cooled.
The injection of gaseous BCl_3 is made through a pipe arriving on the plasma jet axis at 0.2 m in the downstream part of the blast-pipe. The flows are controlled by a standardized tap in stainless steel and teflon (fig. 1).

3. EXPERIMENTAL RESULTS.

The flow of plasma gas (Ar or N_2) varies between 5 and 30 l/mn. The plasma temperature is about 8000 K in argon for a gas flow of 15 l/mn, an electrical power of 5 kW and a static pressure of 30 Pa ; in these conditions the speed is Mach 2.1. In nitrogen : temperature : 5000 K, gas flow : 15 l/mn, power : 12 kW, static pressure : 22 Pa, and Mach 0.9. These values

are constant in a radius of 5 cm around the axis of the plasma jet.
The flow of BCl_3 is 5.10^{-2} l/mn under standard conditions. The deposition time varies from 10 mn up to 5 h. The growing of the coating is about 100 μm/h for boron and 80 μm/h for boron nitrid. The adhesion with the substrate is good for a very thin layer.
These films were caracterized by X ray diffraction and electron beam microprobe analysis. In both cases the coatings are amorphous.
Experiments with a mixture of argon (90 %) and hydrogen (10 %) have been made. This mixture has no influence on the deposit of boron.

4. THEORITICAL CALCULATIONS.

Chemical composition of the plasma.

Theoritical calculations of the composition of plasma for many temperatures and pressures, using the minimization of the Gibbs Energy of the mixture (6) (knowing the Gibbs Energy of formation of each component (7)) have been working out.
So we can foresee the influence of experimental conditions on the quality of the layer (gas flow, temperature, static pressure). The table 1 and fig. 2 gives the main results in the case of Ar, H_2, BCl_3 mixture. A low pressure make the decomposition of BCl_3 and the formation of B. easier. These calculations show the small influence of hydrogen.
In the case of N_2, BCl_3 mixture (see table 2 and fig. 3), we observe the same influence of pressure. The experimental results prove that the formation of boron nitride is a wall reaction (B + N + wall $\rightarrow$ BN). At low pressure, we can accept as true that the plasma composition is frozen and that the wall reaction is influenced by the upstream composition.

Rate deposition.

Another theoritical calculation has been made using the mean reaction :

$$BCl_3 \longrightarrow B + 3\ Cl$$

in a homogeous plasma jet in which the temperature, pressure and velocity are constant. It allows, if we consider the diffusion of the species, the rate of reaction and the conservation of energy, to know the concentrations in each point of the plasma of each chemical component, and so to determine the best position of the substrate.
In this case, an ideal deposition rate of 62 μm/h has been calculated for a BCl_3 injected quantity equal to 5.10^{-2} l/mn. This result agrees well with those obtained in practice for a distance between the point of injection and the substrate of 30 cm.
The thermodynamic calculation indicates that dissociation is complete, on the jet axis, 2 cm beyond the injection point.

5. CONCLUSION.

Plasma deposition in rarefied gas is particularly interesting process for boron and boron nitride thin layers :
- great dimensions pieces can be treated (10 x 10 cm^2),
- deposition and reaction times remain low (10 μm/h),
- substrate temperatures remain low ($<$ 800 K).

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Table 1.
Gas flow : Ar : 10 l/mn, H_2 : 1 l/mn, BCl_3 : 5.10^{-2} l/mn.
Pressure : 3.10^{-4} atn, temperature : 4000^3K.

$Ar = 8.02.10^{-1}$	$H_2 = 1.67.10^{-5}$	$Ar^+ = 2.77.10^{-10}$
$H = 1.78.10^{-1}$	$BCl = 5.02.10^{-7}$	$Cl = 2.28.10^{-10}$
$Cl = 1.45.10^{-2}$	$BH = 2.71.10^{-8}$	$H^{-2} = 1.84.10^{-10}$
$B = 4.70.10^{-3}$	$Cl^- = 2.18.10^{-8}$	$B_2 = 1.12.10^{-10}$
$e^- = 1.15.10^{-4}$	$Cl^+ = 3.93.10^{-9}$	
$B^+ = 1.15.10^{-4}$	$H^+ = 3.01.10^{-9}$	

Concentration lower 10^{-10} : BCl^+, BH_2, BCl_2^+, BCl_2, HCl, BH_3, BCl_3, BCl_2^-, BCl_2^+H, B_2Cl_4, B_2H_6, B_5H_9 , $B_{10}H_{14}$.

Table 2.
Gas flow : N_2 : 10 l/mn, BCl_3 : 5.10^{-2} l/mn.
Pressure : 3.10^{-4} atn, Temperature :4000 K

$N_2 = 9.05.10^{-1}$	$BN = 4.16.10^{-7}$
$N = 9.21.10^{-2}$	$Cl^+ = 2.69.10^{-9}$
$Cl = 1.54.10^{-3}$	$N_2^+ = 1.33.10^{-9}$
$B = 4.43.10^{-4}$	$BCl = 1.28.10^{-9}$
$e^- = 6.97.10^{-5}$	$Cl^- = 3.58.10^{-10}$
$B^+ = 6.97.10^{-5}$	

Concentration lower 10^{-10} : Cl_2, N^+, BCl^+, BCl_2, BCl_2^+, BCl_2^-, BCl_3, B_2, B_2Cl_4.

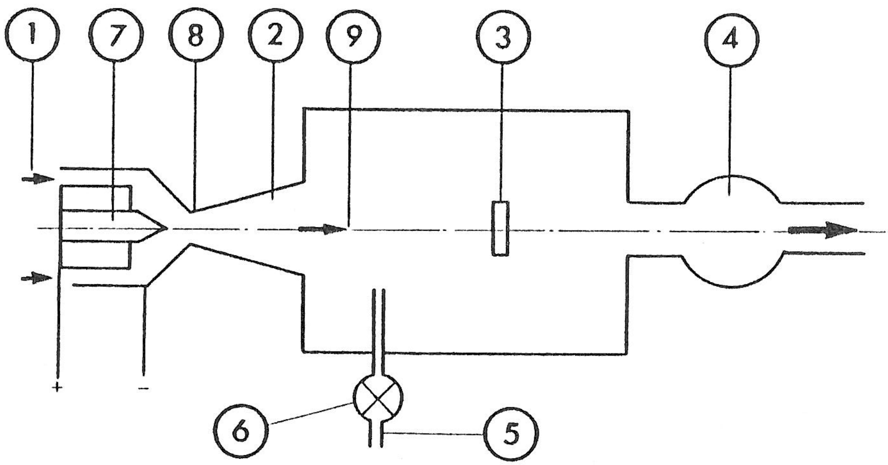

Figure 1 : (1) Gas (2) Blast-pipe (3) Substrate (4) Vacuum pumps (5) Injection pipe (6) Tap (7) Cathode (8) Anode (9) Plasma

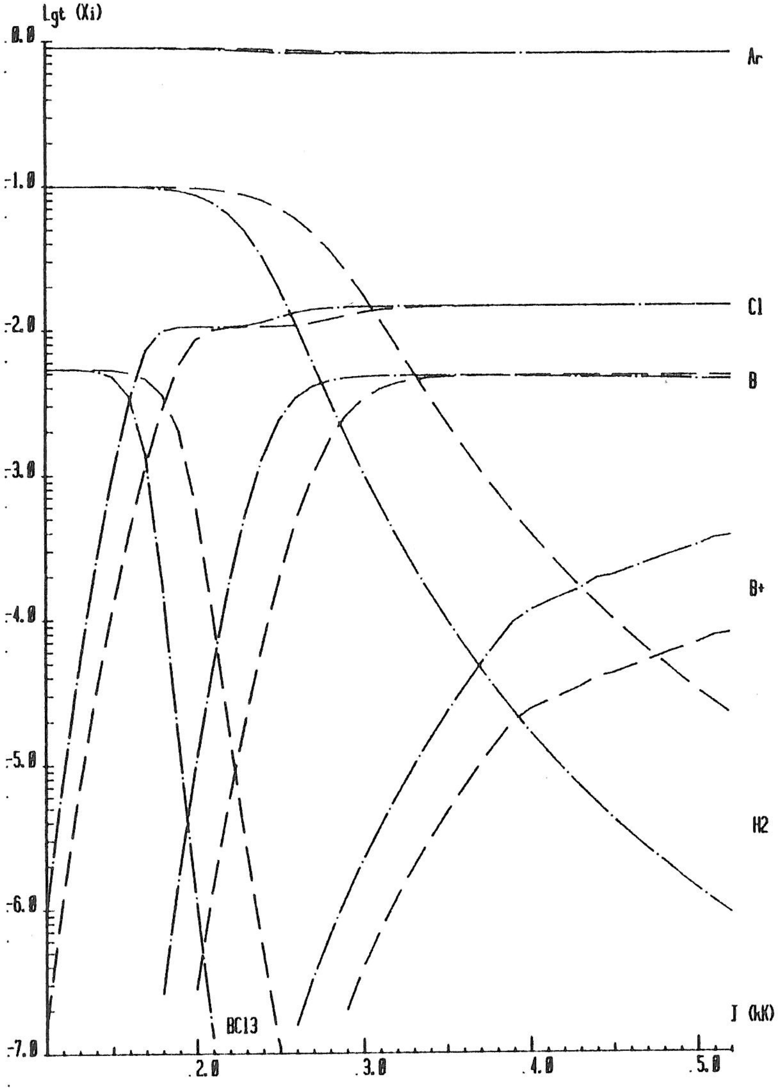

Figure 2 Concentrations versus temperature (AR, H2, BCL3)

—·—·—·— 3.E-4 atm

— — — — 1.E-2 atm

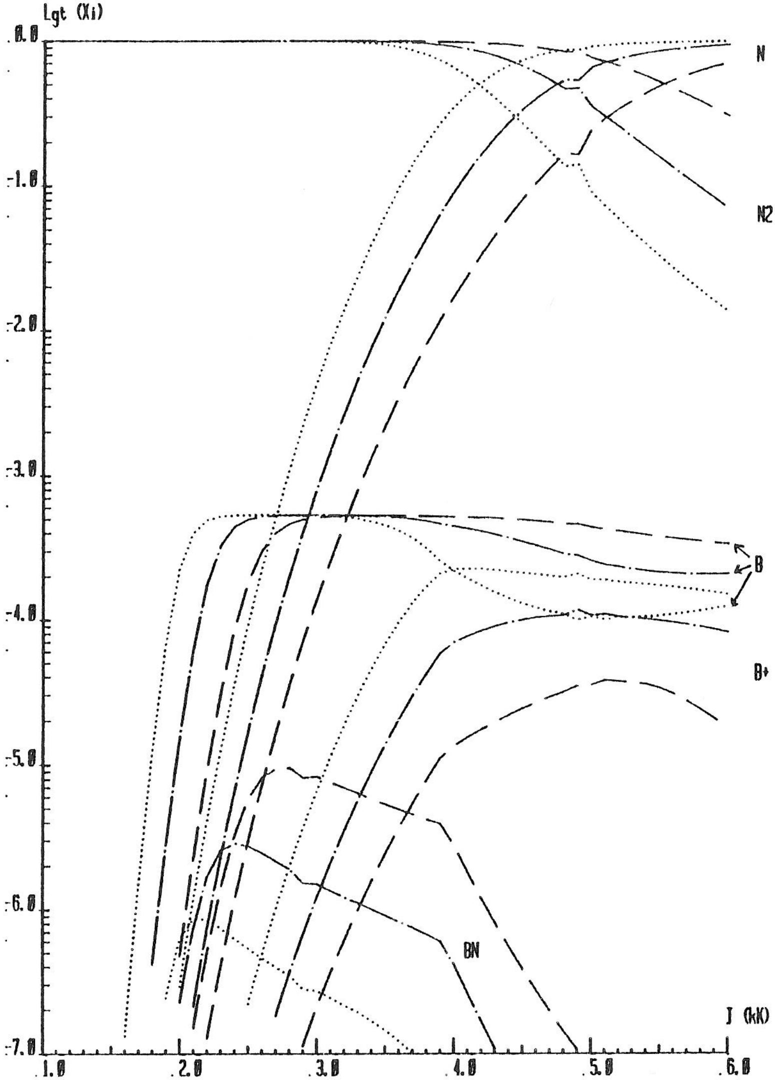

Figure 3 Concentrations versus temperature (N2, BCl3)

—·—·— 3.E-4 atm

— — — 1.E-2 atm

········ 1.E-5 atm