Engineering Boron Nitride Phases via Borazine CVD

Catherine Journet
Thomas Souvignet, Catherine Marichy
Universite Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, France
catherine.journet@univ-lyon1.fr

Boron nitride (BN) is a key material for current and next-generation electronic devices, owing to its wide bandgap, chemical stability, and tunable dielectric properties. Over the past decade, sp^2-hybridized hexagonal BN (h-BN) has become an essential component of graphene-based optoelectronic systems, due to its excellent insulating behavior and low lattice mismatch with graphene.[1,2] More recently, amorphous BN (a-BN) has attracted growing interest, driven by its ultra-low dielectric constant, reported to be as low as 1.16, significantly below typical values for h-BN.[3] Ultra-thin a-BN layers have notably been demonstrated as promising low-k capping layers for copper interconnects in advanced microelectronic architectures.[4]

Exploiting the full potential of BN in electronics, optoelectronics, and spintronics requires precise control over its structural phase, and thus over its physical properties. Among available deposition techniques, chemical vapor deposition (CVD) offers unique versatility for the synthesis of BN thin films with controlled composition and structure. Borazine ($B_3N_3H_6$), a volatile precursor with a stoichiometric B:N ratio, is particularly well suited for BN CVD. However, the deposition mechanisms involved and the influence of key process parameters on the resulting film structure remain incompletely understood.

In this work, BN thin films were deposited by borazine-based CVD on native oxide Si substrates over a wide temperature range (400–1350 °C), while systematically varying the precursor flux and carrier gas. The films were comprehensively characterized using ellipsometry, X-ray diffraction, scanning and transmission electron microscopy, energy-dispersive spectroscopy, X-ray photoelectron spectroscopy, as well as Raman and infrared spectroscopies.

Our results demonstrate that both deposition temperature and borazine flux critically govern film morphology, crystallinity, and bonding configuration. The experimental data point to a competition between two dominant reaction pathways: (i) polycondensation of borazine into oligomeric species and (ii) thermal decomposition into reactive fragments such as BH_3 and NH_3. The balance between these mechanisms is strongly dictated by the CVD conditions, ultimately determining whether amorphous or crystalline BN is formed. Based on these observations, a reaction scheme is proposed to rationalize the phase selectivity observed in borazine-based BN CVD.

References

[1] K. K. Kim et al., ACS Nano, **6**, 8583–8590. **2012**
[2] T. Niu et al., Progress in Surface Science, **90**, 21-45 **2015**
[3] S. Hong et al., Nature, **582**, 511–514 **2020**
[4] C.M. Lin et al. Advanced Materials Technologies, **7**, 2200022 **2022**