Available online at www.sciencedirect.com

ScienceDirect

Surface & Coatings Technology 201 (2007) 8818–8824

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Theoretical determination of accurate rate constants: Application to the decomposition of a single-molecule precursor

Maxim Tafipolsky, Rochus Schmid *

Lehrstuhl für Anorganische Chemie II, Organometallics and Materials Chemistry, Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

Abstract

The ring opening is proposed to be the initial step in the unimolecular decomposition of a single-molecule precursor bisazido (dimethylaminopropyl)gallium (BAZIGA) used in a CVD process of gallium nitride. An efficient Monte Carlo importance sampling technique is developed to estimate the canonical partition functions and absolute entropies therefrom by taking the internal rotor hindrance and all coupling arising from the external and internal rotational degrees of freedom into account. This allows the estimation of the free energy difference in the ring opening process of BAZIGA to be made.

Canonical flexible transition state theory is applied to the radical Ga–C bond homolysis in the unimolecular decomposition of BAZIGA. The limiting high-pressure rate constant is calculated using a simple model for the potential energy surface based on density functional calculations.

Keywords: Gallium nitride; CVD; Single-molecule precursor; Flexible transition state theory; Rate constant

1. Introduction

The ternary, wide-band gap, group-13 nitride semiconductors of the type AlGaN and InGaN have been established as important materials for a broad variety of applications including optoelectronic devices, particularly for short-wavelength LEDs and laser diodes. Recently, bisazido(dimethylaminopropyl) gallium (BAZIGA), **1** (see Fig. 1), has been shown to be a very attractive single molecule precursor for the chemical vapor deposition (CVD) of gallium nitride [1].

The modeling of many chemical processes, including combustion, catalysis, polymerization, etc., requires a detailed knowledge of entropic changes occurring during the reaction. Therefore, partition functions are needed to calculate various thermodynamic properties of a system. The entropic contributions to free energies can be quite substantial especially at elevated temperatures and when large molecules are involved. In CVD processes, these contributions can play an important role in the unimolecular decomposition of especially large precursor molecules at elevated temperatures. For the determination of gas-phase rate constants this can become as important as the accuracy of the calculated potential energy surface (PES). For molecules, where several hindered internal rotations are present, the usual harmonic oscillator, rigid-rotator approximation is no longer valid. A proper treatment should take both the internal rotor hindrance and all coupling arising from the external and internal rotational degrees of freedom into account.

Computational fluid dynamics (CFD) is widely used in modeling of the whole process of the gallium nitride deposition in a reactor [2], where, among other things, the rate constants for the elementary reactions should be supplied.

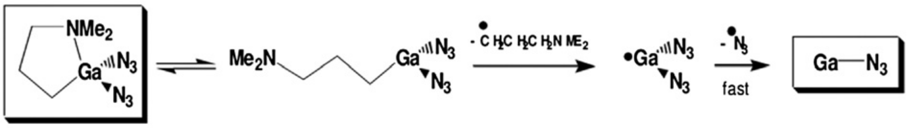
In our efforts to elucidate the mechanism and rate constants of a CVD process using this particular single-molecule precursor, it is argued [3] that the ring opening (going from **1** to **2**) is the most

---

* Corresponding author.
E-mail address: Rochus.Schmid@ruhr-uni-bochum.de (R. Schmid).

0257-8972/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2007.04.054

probable initial step in the unimolecular decomposition of **1**. The whole decomposition process for BAZIGA can be represented by the following scheme:



Previously [3] it has been shown that at temperatures relevant for the CVD process (1000 °C) the entropic contribution from the rotational degrees of freedom of the open arm of BAZIGA, **2**, obtained from a separable (uncoupled) treatment of the external and internal rotations differs from that based on the rigid rotor-harmonic oscillator approximation. Below we develop a fully coupled treatment of the rotational degrees of freedom for **2**. Next, we describe the application of the canonical flexible transition state theory (CFTST) to the radical Ga–C bond homolysis by treating transitional modes via efficient numerical integration. The configuration integral over the transitional modes is evaluated using a Monte Carlo technique with stratified sampling in the temperature range from 400 to 1000 K.

Whereas the rigid rotor-harmonic approximation seems quite reasonable for **1**, this is not the case for the open arm, **2**, due to the presence of multiple large amplitude internal rotations about single bonds. A fully coupled approach developed recently for a non-rigid chain molecule [4] is adopted here for the calculation of the rotational entropy for the open arm. This approach has been recently applied by us [3] for the estimation of rotational entropies for a number of small straight chain *n*-alkanes from ethane to octane. In the present work, we use the technique now for the first time for a much more complicated metal-organic CVD precursor. The approach is based on an efficient (importance sampling) Monte Carlo integration of the configurational phase space, thus accounting for all relevant rotamers. The configurations must be Boltzmann weighted using a potential energy term, which is calculated from an empirical molecular mechanics force field. It must be sufficiently accurate to properly model the steric hindrance in the different configurations. The influence of the methodology to calculate the rotational partition function on the free energy difference between the closed (**1**) and the open (**2**) form of BAZIGA will be discussed.

2. Computational details

2.1. Ring opening in BAZIGA

2.1.1. Canonical partition function

Among the methods available for non-linear polyatomic molecules, a semiclassical approach developed long ago by Pitzer et al. [5,6] seems to be the most attractive one, especially when thermodynamic functions are required at elevated temperatures. The expression for the classical rotational partition function is well-known and is given by:

$$Q_{\mathrm{rot}} = \frac{8\pi^2}{\sigma}\frac{(2\pi k_B T)^{(n+3)/2}}{h^{(n+3)}}\int_0^{2\pi}\ldots\int_0^{2\pi}\sqrt{|A(\phi)|}e^{-\frac{V(\phi)}{k_B T}}d\phi, \quad (1)$$

where n is the number of internal rotational degrees of freedom, $|A|$ is the determinant of the generalized inertial tensor matrix (GIT); $V(\phi)$ is the hindering potential for the internal rotation; $\phi=(\phi_1, \phi_2,\ldots,\phi_n)$ is a vector of the

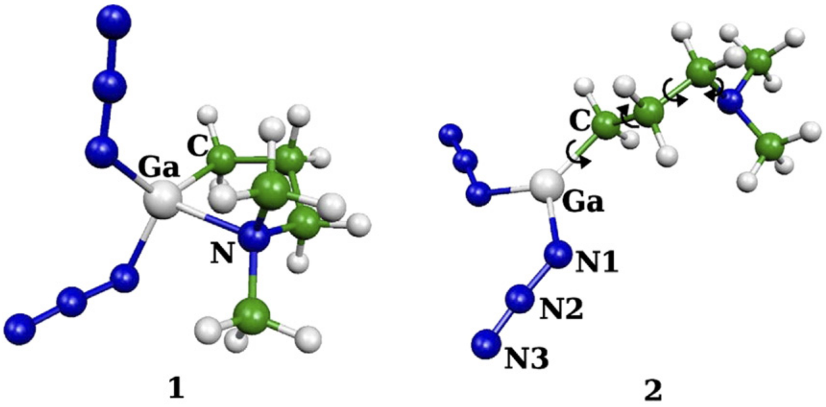


Fig. 1. Molecular structures for closed (**1**) and open (**2**) BAZIGA.