

ON THE MECHANISM OF METAL COMBUSTION IN NITROGEN

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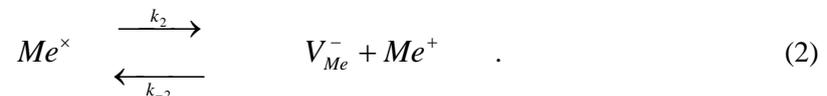
In recent years a growing need has appeared for high power electronic devices capable of operation at high temperatures and caustic environments. This led to renewed efforts directed towards III-V nitrides research.

The kinetics of the high-temperature Ti, Zr, Nb and Ta nitridation at the early combustion stages was studied in details [1-3]. It was revealed [3] that the rate of the TaN film growth is proportional to the power of $-1/2$ for the nitrogen pressure. Therefore the authors concluded that neutral nitrogen vacancies are mainly responsible for mass transfer during high-temperature tantalum nitridation. The same mechanism of nitrogen diffusion is implied for the other metals [4,5]. Nevertheless, there are data contradicting the conclusion [3]. The data on the defects and transport properties of nitrides [6] show that nitrogen diffusion and nitride formation are limited by transfer of metal vacancies in nitride. These vacancies are usually charged negatively. Moreover, like in oxygen [7,8] self-generation of a transient electric voltage was observed during the Ti combustion in nitrogen [9]. One cannot explain this voltage taking into account only the neutral vacancies.

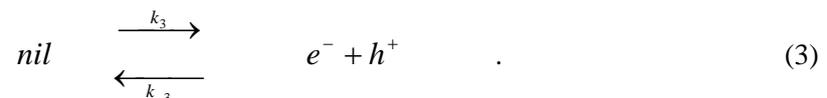
We suggest a mechanism of defect formation in nitrides through metal vacancies. The ambient gaseous nitrogen is adsorbed on the nitride-nitrogen surface via the reversible reaction



Interstitial metal cations and metal vacancies are formed in the nitride lattice by the reactions



Simultaneously, electron-hole pairs are generated via thermal ionization



The different diffusion rates of the charge carriers (Me^+ , e^- and V_{Me}^- , h^+) produce an electric charge in the nitride shell. The metal cations and electrons are consumed or produced by a reaction at the metal-nitride interface:



Using this mechanism in model [10,11] we have succeeded in explanation of the electrical field generation during the high-temperature nitridation of metal particles [9] and implicitly confirm the data [6]. The discrepancy with the conclusion [3] is discussed.

Preliminary calculations of the model [10,11] modified for combustion in nitrogen with the proposed mechanism of defect formation are presented in Fig. 1. One can see that the characteristic time scale of the surface electric potential is much less than those of temperature, conversion degree and concentration of the adsorbed nitrogen. The maximum of the surface electric potential is attained before the temperature and concentration have reached their maximums. These two results are completely similar to those for oxygen combustion [10,11] and can be explained by the non-

equilibrium concentrations of metal vacancies and electron holes during the initial nitridation stage. The surface defect concentrations attain the equilibrium values by the time of the maximum temperature has been achieved. This led to a drop in the surface electric potential. In contrast to oxidation [10,11] the activation energies of nitrogen adsorption as well as the adsorption rate constants have negligible effect on the surface potential form and amplitude. The reason is that the metal-nitride interface but not the particle surface serves as the main source of defects during nitridation. Therefore, the changes in the surface kinetics have no such effect like on the formation of oxides with a mixed electronic-ionic conductivity [10,11].

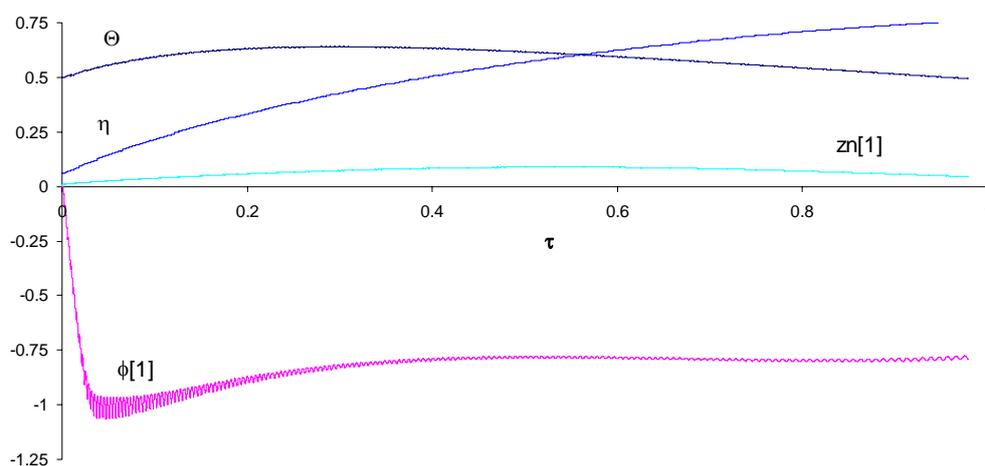


Fig. 1. Typical transient temperature (Θ), conversion degree (η), concentration of the surface adsorbed nitrogen ($zn[1]$) and surface electric potential ($\Phi[1]$) during combustion of a metal particle in nitrogen

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