Optical emission spectroscopy of the flowing afterglow of a microwave N_2/O_2 plasma used for the modification of GaN nanowires

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Abstract
Optical emission spectroscopy was used to characterize the flowing afterglow of a microwave plasma in N_2/O_2 gas mixtures used for the modification of GaN nanowires. Spatially-resolved investigations revealed an unexpected minimum of the emission intensity from the second positive system of N_2; a feature that was ascribed to substrate reactions which played an important role on the population dynamics of the $N_2(A)$ state responsible for the creation of emitting $N_2(C)$ levels.

1. Introduction
There has been an increasing interest in the use of flowing afterglows in N_2/O_2 gas mixtures for the modification of heat-sensitive materials such as polymers for various technological applications, in particular the sterilization of medical instruments [1]. We have recently started investigations on the plasma-induced functionalization of GaN nanowires to tune their emission properties for advanced optoelectronic device applications. In this preliminary work, we examine the evolution of active species in the flowing afterglow of a microwave N_2/O_2 plasma by optical emission spectroscopy.

2. Experimental set-up and diagnostics
The apparatus consists of a 0.6 cm inner diameter (0.8 cm outter diameter), 38.1 cm long fused silica tube connected to a stainless processing chamber, with the substrate being located at 3.4 cm from the end of the tube. The plasma is sustained in N_2/O_2 gas mixtures by a 2450 MHz propagating electromagnetic surface wave lauched using a surfatron [2]. For all experiments, the operating pressure is fixed to 0.8 Torr. The power is varied between 30 and 70 W, producing plasma columns with lenghts in the 1.6-3.1 cm range. The relatively high nitrogen gas flows (100-200 sccm) create a flowing discharge afterglow down to the substrate surface where the plasma-induced modification occurs. Spatially-resolved optical emission spectroscopy is used to examine the influence of the operating parameters on the spatial distribution of active species in the afterglow region.

3. Results and discussion
Figure 1 shows the influence of the injected power in pure N_2 on the bandhead emission intensity from the second positive system (SPS) of N_2 ($C^3\Pi_u$,v'=0$\rightarrow B^3\Pi_g$,v''=0) at 337 nm and from the first negative system (FNS) of N_2^+ ($B^2\Sigma_u^+$,v'=0$\rightarrow X^2\Sigma_g^+$,v''=0) at 391 nm. For these experiments, the wave launcher was moved such that the distance between the end of the plasma column and the substrate was kept constant at 17.7 cm. Both emission intensities increase with power but the increase from the FNS was more prominent (337 nm-to-391 nm intensity ratio decreases with power). Assuming that the $N_2(C)$ state giving rise to the emission at 337 nm is populated by pooling reactions between $N_2(A)$ metastables (reaction rate k_1) and that the $N_2^+(B)$ state leading to the emission at 391 nm is created by either (*i*) electron-impact excitation of $N_2^+(X)$ (reaction rate k_2) or by (*ii*) collisions between N_2(X, v'>11) and $N_2^+(X)$ (reaction rate k_3), the 337 nm-to-391 nm emission intensity ratio becomes

$$\frac{I_{337nm}}{I_{391nm}} \propto \frac{k_1\left[N_2(A)\right]^2}{k_2\left[N_2^+(X)\right]\left[e\right]+k_3\left[N_2^+(X)\right]\left[N_2(X,v'>11)\right]}, \qquad (1)$$

where the brackets refer to the number density of the corresponding species. We have determined the vibrational distribution of N_2 using the emission from the Δv=-4 sequence of the SPS in the 415-436 nm range [3]. Assuming that the density of vibrational states follows a Boltzmann distribution, we find a fairly constant vibrational temperature T_{vib}=4800±200 K. From this result, we have extrapolated $[N_2(X,v'=11)]/[N_2(X,v'=0)] \sim 10^{-2}$, which is much higher than the expected electron-to-neutral number density ratio, thus indicating that electron-impact excitation can be neglected in Eq. (1).

The spatial distribution of the plasma emission in the flowing afterglow region is shown in Fig. 2. While the emission intensity from the FNS decrease monotonously when going from the plasma region to the substrate region, an unexpected minimum is oberved for the SPS of N_2 near z=1.7 cm. Based on Eq. (1), the stronger emission from $N_2(C)$ states near the substrate can probably be attributed to surface reactions producing a higher concentration of $N_2(A)$. One possible reaction scheme could be the heterogenous recombination of N atoms $N + N + N_2 \rightarrow N_2(B,\nu'=11) + N_2$, which produces $N_2(B)$ states leading to the emission from the N_2 first positive system ($B^3\Pi_g$-$A^3\Sigma_u^+$). The lower level being the $N_2(A)$ metastable, this state can then populate the $C^3\Pi_u$ level. Measurements for various substrates, and thus various surface recombination probabilities, are in progress.

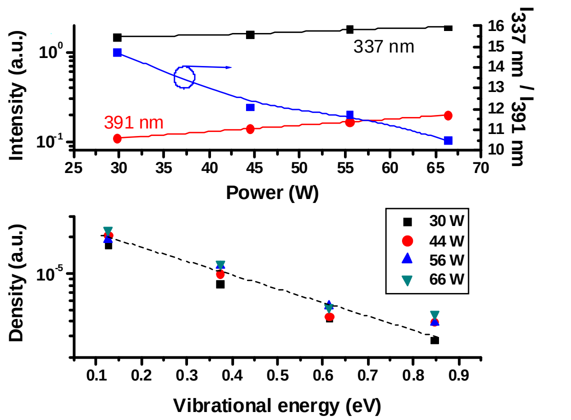

Fig. 1 : (a) Influence of power on the emission intensity from the SPS of N_2 at 337 nm and from the FNS of N_2^+ at 391 nm in pure N_2 plasmas for z=0 cm. The ratio of these two bands is also shown. (b) Influence of power on the energy distribution of N_2 vibrational states.

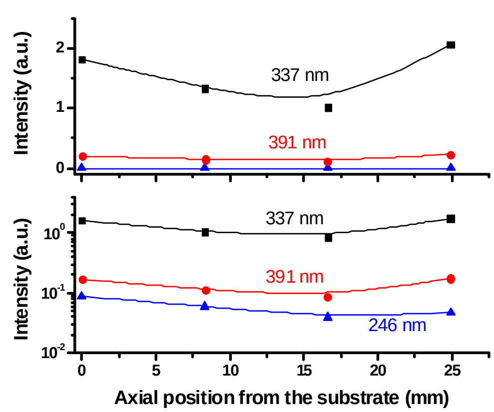

Fig. 2 : Axial distribution of the emission intensity from the SPS of N_2 at 337 nm, from the FNS of N_2^+ at 391 nm, and from the NOγ system at 246 nm in (a) 30 W, pure N_2 plasma and (b) 30 W, N_2 + 0.5 % O_2 plasma.

In the presence of small amounts of O_2 in N_2, an important emission from the NO_γ system between 200 and 300 nm was observed. Given their high-energy (4.1-6.2 eV), these photons are likely to play a very important role in the surface modification dynamics of GaN nanowires. An interesting feature was that the emission intensity from NO_γ increased continuously as more O_2 was added to the N_2 plasma, at least up about 10% O_2 in N_2+O_2 (not shown). This is in sharp contrast to the results presented in ref. [1] in which NO emission exhibited a maximum near 0.5 % of O_2.

4. Conclusions

We have analysed the characteristics of the flowing afterglow of a reduced-pressure N_2/O_2 plasma sustained by microwave electromagnetic fields using spatially-resolved optical emission spectroscopy. An unexpected minimum of the emission intensity from the second positive system of N_2 was observed near the substrate surface, a feature that was ascribed to the heterogeneous recombination of N atoms on the substrate which seems to play an important role on the population dynamics of the $N_2(A)$ level responsible for the creation of emitting $N_2(C)$ states.

5. References

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