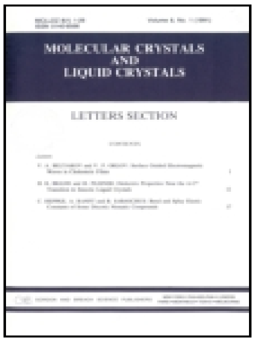

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Photoisomerization of Azophenylcarbazole Self-assembled Monolayer on GaN Studied by Kelvin Probe

V. BIKBAJEVAS,[1] A. KADYS,[1] R. TOMAŠIŪNAS,[1,*]
R. PŪRAS,[2] S. URNIKAITĖ,[3] AND V. GETAUTIS[3]

[1]Institute of Applied Research, Vilnius University, Lithuania
[2]Semiconductor Physics Department, Faculty of Physics, Vilnius University, Lithuania
[3]Kaunas University of Technology, Lithuania

*Self assembled monolayers of two fabricated azophenylcarbazoles on GaN epitaxial layers were obtained. Isomerization of the azo derivatives has been accomplished by illumination with wavelength of 440 nm, which coincides with their absorption maxima. The process has been observed in situ by Kelvin probe. A few parameters for azophenylcarbazoles (**V-650** and **V-728**) of* trans-cis *switching such as difference between work function in* trans *and* cis *state and time constant for* trans-cis *and* cis-trans *isomerizations have been determined.*

Keywords Isomerization; azophenylcarbazole; gallium nitride; Kelvin probe

1. Introduction

Controlled modification of the semiconductor surface properties is an attractive strategy for the development of new technologies with possible applications in molecular electronics and stable hybrid molecular-semiconductor devices. Molecular switches are promising systems for such a route, since they possess the ability to undergo reversible changes between different molecular states and accordingly molecular properties by excitation with light or other external stimuli [1]. The possibility to design molecules with specific functional properties opens the perspective to use molecules as building blocks for integrated functional devices [2].

For realization of this vision problem of attachment a large number of molecular switches to a solid surface in a way so that robust and efficient switching remains possible need to be solved. GaN has many characteristics that could make it an exceptional material for this purpose. It is suited for operation in harsh environments, such as high temperature, high pressure, or corrosive ambients. GaN is not etched by any acid or base at temperatures below a few hundred degrees. It possesses high electron saturation velocity, and simple integrates with the existing GaN-based light-emitting diode, detectors, and wireless communication chips and can be used as a transducer for a sensor [3]. Recently, azo compounds have been studied with immense interest for their unique isomerization effect. [4–5].

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[*] Address correspondence to R. Tomašiūnas, Institute of Applied Research, Vilnius University, Lithuania. E-mail: rolandas.tomasiunas@ff.vu.lt

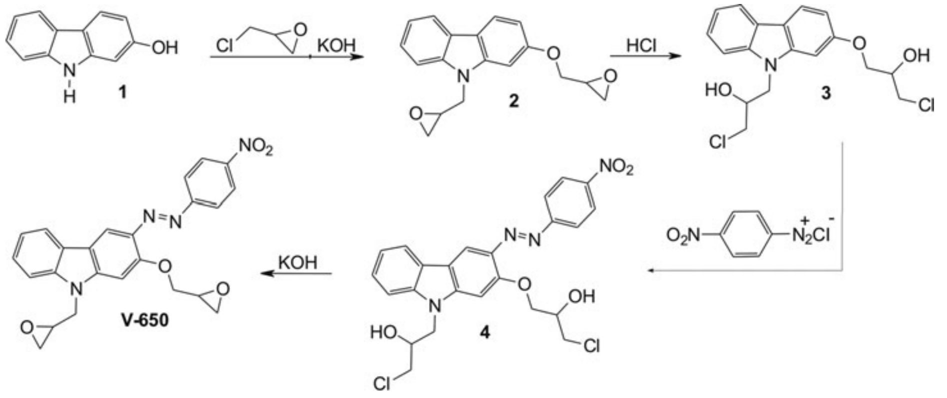

Figure 1. Synthesis route to the azo derivative **V-650**.

The main objective of this study comprises the functionalization of GaN surface by azo derivatives for their photoisomerization phenomenon via excitation with light at appropriate wavelengths. Thereby, the molecules are interconverted reversibly between *trans* and *cis* states.

2. Experimental

2.1 Samples

The synthetic procedure for azophenylcarbazole-based structures, hereinafter referred to as **V-650**, is summarized in Fig. 1. Thus, by interaction of 2-hydroxy-9*H*-carbazole (**1**) with epichlorohydrin in the presence of potassium hydroxide 9-(2,3-epoxy)propyl-2-(2,3-epoxy)propoxy-9*H*-carbazole (**2**) was obtained in good yields. Diepoxide **2** upon oxirane ring opening reaction with HCl yielded 9-(3-chloro-2-hydroxy)propyl-2-(3-chloro-2-hydroxy)propoxy-9*H*carbazole (**3**). The azo dye 9-(3-chloro-2-hydroxy)propyl-2-(3-chloro-2-hydroxy)propoxy-3-(4-nitrophenyl)azo-9H-carbazol (**4**) was prepared by coupling reaction of compound **3** with diazonium salt prepared from 4-nitroaniline. Then, isolated intermediate **4** was treated with KOH to obtain the desired monomer 9-(2,3-epoxy)propyl-2-(2,3-epoxy)propoxy-3-(4-nitrophenyl)azo-9*H*-carbazole (**5**) [6].

The azophenylcarbazole-based structure, hereinafter referred to as **V-728**, was obtained by the coupling reaction of carbazole (**1**) with diazonium salt of 2-chloro-4-nitroaniline (**2**) followed by treatment of the resulting 3-(2-chloro-4-nitrophenylazo)-9*H*-carbazole (**2**)

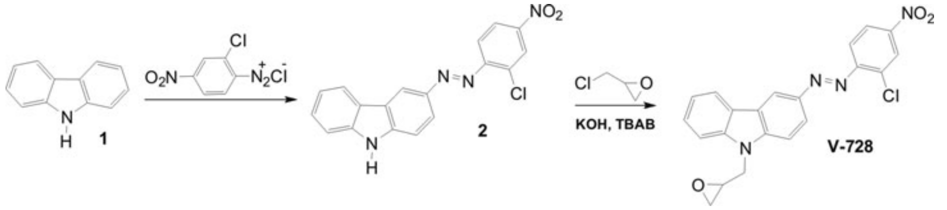

Figure 2. Synthesis route to the azo derivative **V-728**.

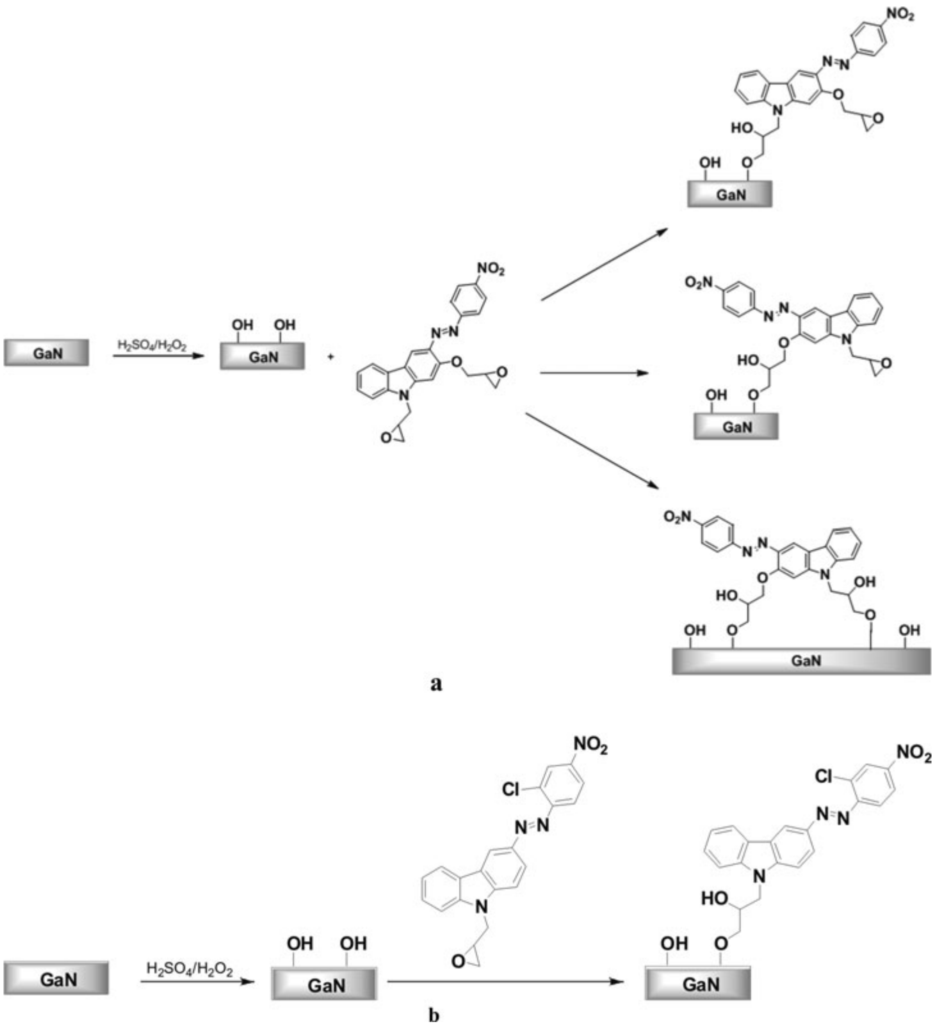

Figure 3. Schematic representation of the process of azophenylcarbazole SAM formation on GaN (**a**) **V-650**, (**b**) **V-728**.

with epichlorohydrin in the presence of potassium hydroxide and tetrabutylammonium bromide (TBAB) as a catalyst according to the procedure described in [7]. The 3-(2-chloro-4-nitrophenylazo)-9-(2,3-epoxypropyl)-9*H*-carbazole (**V-728**) was obtained in form of a red powder with very good yield (Fig. 2).

The GaN epitaxial layers were grown by metal-organic chemical vapor deposition (MOCVD) in the AIXTRON close coupled showerhead 3 × 2 inch capacity flip-top reactor. The samples were grown on *c*-plane of sapphire wafers. GaN was not intentionally doped but possessed *n*-type with $n = 5{\cdot}10^{17}$ cm^{-3} and $\mu = 250$ cm^2/(V·s) at room temperature.

The surface of GaN was hydroxylated by wet chemical treatment in piranha etch (H_2SO_4: H_2O_2 = 3:1). The azophenylcarbazole self assembled monolayer (SAM) [8] formation was performed by immersing the samples in a solution of the above-mentioned chemical substances in THF for 12 hours (Fig. 3).

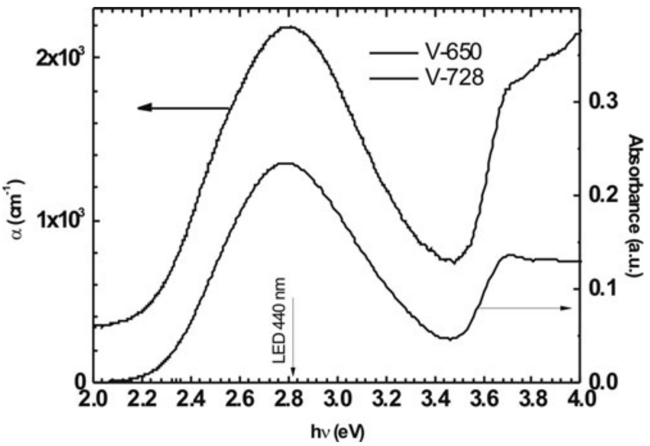

Figure 4. The absorption spectra of azo derivatives **V-650**, and **V-728**.

2.2 Technique

During the process of *trans-cis* isomerization the geometry of the azophenylcarbazole molecules changes that leads to modification of their dipole moments [9]. Therefore, the work function of the GaN surface with SAM of azo derivatives depends on their states and can be used as status indicator of the system [10] estimated using the oscillating Kelvin probe technique [11]. Actually, this method enables to obtain not the absolute value of the work function, but the difference between the work functions of GaN surface with SAM and gold probe electrode.

The absorption maxima of azophenylcarbazoles **V-650** and **V-728** were found to be located in the range of 443–445 nm (Fig. 4), hence, we applied a LED illumination with $\lambda = 440$ nm for photoisomerization of the azo derivatives from *trans* to *cis* state. The measurements *in situ* were performed by Kelvin probe method in air at room temperature.

3. Results

Although the photon energy of 440 nm light (2.8 eV) is smaller than GaN band gap (3.4 eV), such photons change filling of the surface states in GaN what causes modification of surface barrier and correspondingly the work function [12–13]. However, the work function varies only slightly during the periods of illumination and of the dark (Fig. 5). Therefore, the observed changes in work function during illumination and after it for GaN with SAM have to be attributed to the isomerization of the azophenylcarbazole (Figs. 6, 7). At the same time the values of the work function after each cycle of dark-illumination cycle have undergone a change while the difference between GaN work function in the dark and during the illumination remain constant. It is conceivable that the observed results are associated with photo-induced adsorption-desorption of oxygen during illumination [13–14]

The process of *trans-cis* photoisomerization and thermal *cis-trans* recovery in the dark for azo-SAM **V-650** is well observed in Fig. 6. The **V-650** in *trans* state was irradiated reaching almost a quasistationary state indicating a balance between the two processes, then, left in the dark for thermal recovery. The obtained experimental results were fitted by

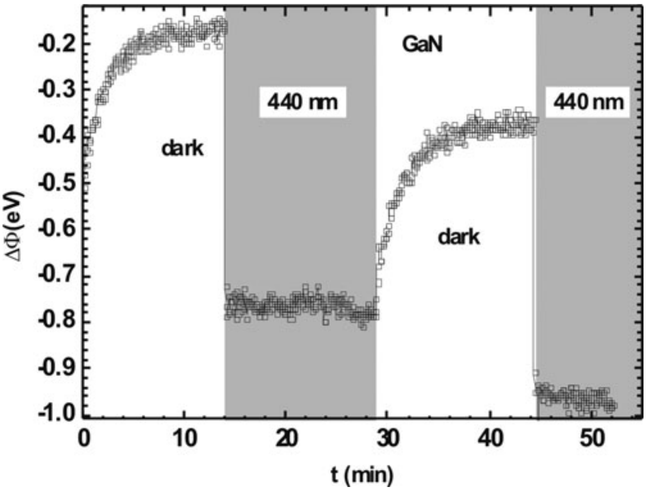

Figure 5. Work function variation corresponding to surface barrier of GaN modification due to 440 nm illumination recorded *in situ* by Kelvin probe experiment.

following exponential expressions:

$$\Delta\Phi(t) = \Delta\Phi_{cis} - \Delta\Phi_{trans-cis} \times \exp\left(-\frac{t - t_0}{\tau_{trans-cis}}\right) \qquad \text{for } trans - cis$$

and

$$\Delta\Phi(t) = \Delta\Phi_{trans} + \Delta\Phi_{trans-cis} \times \exp\left(-\frac{t - t_0}{\tau_{cis-trans}}\right) \qquad \text{for } cis - trans$$

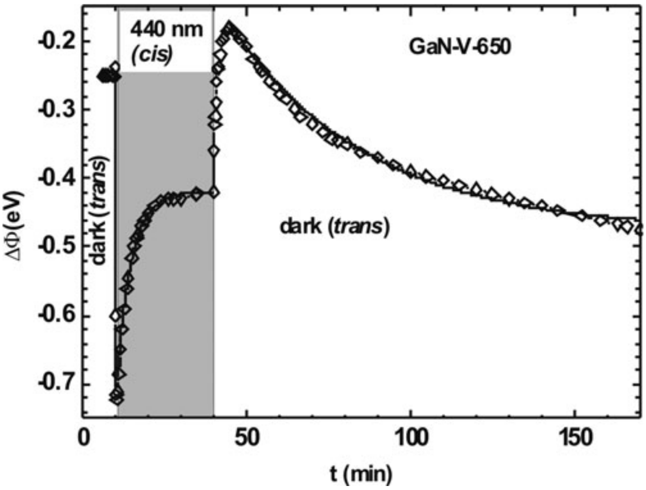

Figure 6. Work function variation corresponding to surface barrier of GaN modification, while photoisomerization of azophenylcarbazole **V-650** from *trans* to *cis* due to 440 nm illumination and cis-trans back recovery recorded *in situ* by Kelvin probe experiment. Line – the best fit for the experimental points (see text for details).

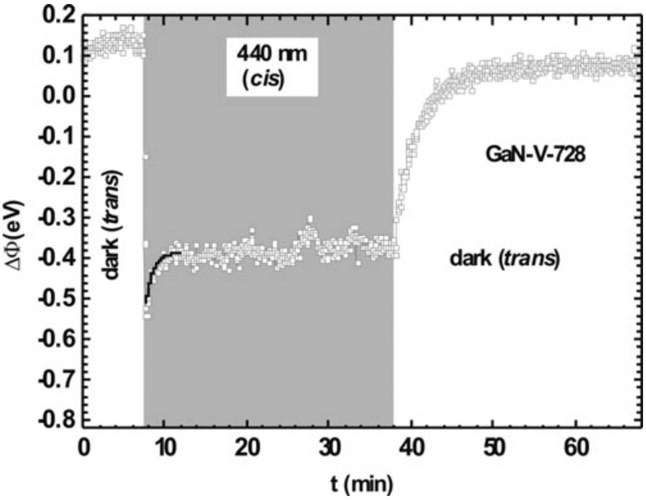

Figure 7. Work function variation corresponding to surface barrier of GaN modification, while photoisomerization of azophenylcarbazole V-728 from *trans* to *cis* due to 440 nm illumination and cis-trans back recovery recorded *in situ* by Kelvin probe experiment. Line – the best fit for *trans* to *cis* transition.

isomerisations [15]. Some parameters of **V-650** isomerization have been determined, namely, the difference between the work function in *trans* and *cis* states, $\Delta\Phi_{trans\text{-}cis} = 0.3$ eV, the time constants for *trans-cis* switching, $\tau_{trans\text{-}cis} = 4.5$ min., and *cis-trans* recovery, $\tau_{cis\text{-}trans} = 42.4$ min. The work function value for the *trans* state before and after illumination does not coincide. It depends upon the fact that the work function of GaN changes (Fig. 5).

In the case of azo-SAM **V-728** fast *trans-cis* switching can be easily distinguished (Fig. 7, $t = 7.5$–10 min.). By fitting some parameters of **V-728** isomerization have been determined, namely, difference between work function in *trans* and *cis* states, $\Delta\Phi_{trans\text{-}cis} = 0.12$ eV, time constants for *trans-cis* switching, $\tau_{trans\text{-}cis} = 0.9$ min. However, reverse transition could not be detected. It is conceivable that the observed result is caused by a relative fast *cis-trans* switching, whereas the change of work function is determined by GaN to a greater extent.

4. Conclusions

The performed study testifies that the SAM of two azophenylcarbazoles (**V-650** and **V-728**) on the GaN surface was obtained. The isomerization of the azo derivatives accomplished by resonant illumination (wavelength coincident with absorption maximum) was observed *in situ* by Kelvin probe experiment. A few parameters for the azophenylcarbazole *trans-cis-trans* switching such as difference between work function in *trans* and *cis* and time constant for *trans-cis* and *cis-trans* transitions have been determined.

Acknowledgments

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