Vass Á, Tálas E, Pászti Z, Drotár E, Sajó I, Tompos A
Preparation and characterization of GaN-ZnO photocatalyst
In: Szélpál Sz (szerk)
Innovation in science: Doctoral student conference 2014.
Szeged, Magyarország, 2014.05.02-2014.05.03.
Szeged: Doktoranduszok Országos Szövetsége, 2014. pp. 72-73.
(ISBN:978-963-9970-52-6)

PREPARATION AND CHARACTERIZATION OF GaN-ZnO PHOTOCATALYSTS

Ádám Vass, Emília Tálas, Zoltán Pászti, Eszter Drotár, István Sajó, András Tompos

Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, 1519 Budapest, P.O.Box 286, vass.adam@ttk.mta.hu

SUMMARY

Co-precipitation followed by nitridation was applied to prepare GaN-ZnO solid solutions suitable for photocatalysis. Characterization of the samples by XRD, EDX, XPS techniques shows that only partial nitridation with small ZnO incorporation took place.

1. INTRODUCTION

Photocatalytic hydrogen production is a promising approach for storing solar energy as a chemical energy. In order to effectively utilize solar energy, new materials working under visible light are needed. Recently GaN-ZnO solid solutions have been developed for decomposition of H_2O into H_2 under visible light irradiation (Maeda, 2005). While GaN (3.4eV) and ZnO (3.2eV) are wide band gap semiconductors of white color, GaN-ZnO obtained from high temperature nitridation of the mixture of Ga_2O_3 and ZnO is yellow with decreased band gap depending on the ZnO content (Maeda, 2010). Our aim was to find new preparation method for GaN-ZnO solid solution. The assumption was that homogeneous distribution of the components is favorable to form a solid solution, so application of different co-precipitation techniques using different metal precursors was studied.

2. MATERIALS AND METHODS

All chemicals were Sigma products. Samples (Table 1) were prepared from nitrates (1), oxides (2) and chlorides (3), respectively. The precursors were dissolved in urea containing distilled water. The mixture was kept under continuous shaking at 130°C for additional 4 h in a closed rotary shaker. The decomposition of urea resulted in alkaline pH thus the dissolved Ga and Zn co-precipitated with forming hydroxides. Shaking was continued in open shaker for 4 h at 130°C. Then the precipitate was washed until neutral pH and dried in oven at 80°C overnight. Finally it was treated in NH_3 flow for 10 h at 800°C. Samples were characterized by means of diffuse reflectance UV-Vis spectroscopy, SEM, EDX, XRD and XPS techniques.

3. RESULTS AND DISCUSSION

After nitridation the color of the samples was pale yellow (2) and grayish yellow (1, 3). According to the UV-Vis measurements the adsorption edges shifted to the visible region (not shown). The SEM images (Fig. 1.) indicate that the samples consisted of particles with uneven size distribution up to the size of 300 μm. These particles resulted from cementation and the aggregation of the crystalline nanoparticles with average particle size of 10-25 nm (based on XRD). The XRD patterns (Fig. 2A) show that before the nitridation the coprecipitated samples contained GaOOH (1, 3), $ZnGa_2O_4$ (1, 3), ZnO (3), while the blank experiment with the mechanical mixture of Ga_2O_3 and ZnO (2), contained only the starting materials. After nitridation only GaN was detected in all samples (Fig. 2B). We were not able to distinguish the solid solution or separate ZnO phase, because both GaN and ZnO crystallize in wurtzite structure with very similar XRD pattern (Fig. 2C). Peak broadening indicated the

presence of amorphous phases, especially in sample 3. This idea was confirmed by the XRD based Zn/Ga atomic ratios of the un-nitridated samples, which exceed the introduced values (Table 1). This finding can be explained only with a Ga containing phase un-visible for XRD. The EDX based Zn/Ga ratio of the nitridated samples was lower than the introduced one (Table 1). The Zn deficiency is particularly evident in sample 3 where EDX showed extremely low homogeneity, too. It is very likely, that some part of the Zn was removed during the preparation *i.e.* it was washed out and/or volatilized during the high temperature nitridation (Maeda, 2005). These processes were dominant on the surface of the particles. The XPS results showed high degree of surface depletion of Zn (Table 1), oxynitride formation with small Zn incorporation and the presence of significant amount of Ga_2O_3 in all samples.

Table 1. Influence of the different metal precursors on the Zn/Ga ratio

Sample	Precursors		$Zn/Ga_{introduced}$	$^{a}Zn/Ga_{XRD}$	$^{b}Zn/Ga_{EDX}$	$^{b}Zn/Ga_{XPS}$
	Ga	Zn				
1	$Ga(NO_3)_3$	$Zn(NO_3)_2$	0.087	0.102	0.081	0.033
2	Ga_2O_3	ZnO	0.136	0.157	0.114	0.023
3	$GaCl_3$	$ZnCl_2$	0.190	0.595	0.041	0.005

[a]before nitridation at 800 [o]C, [b]after nitridation at 800[o]C

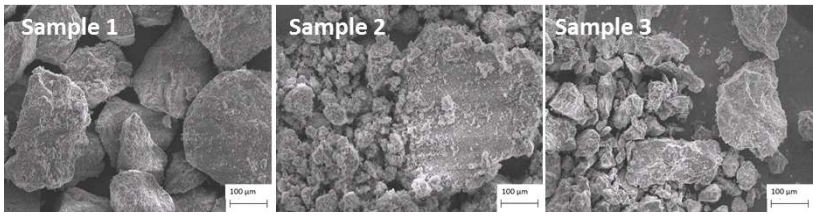

Figure 1. SEM image of samples after nitridation

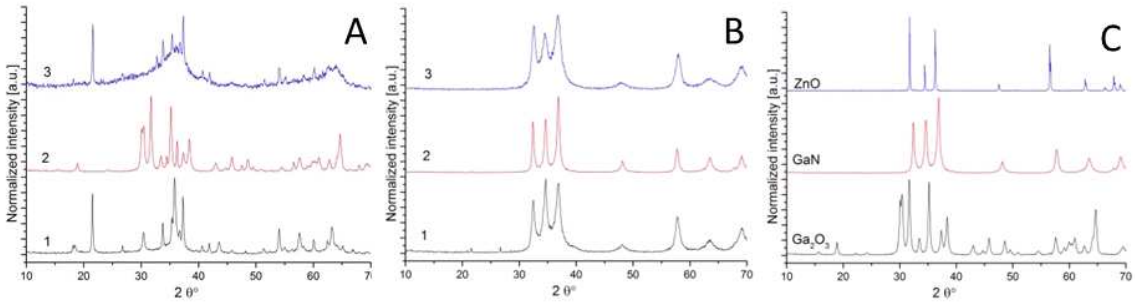

Figure 2. XRD pattern of samples1,2 and 3; A: before nitridation, B: after nitridation C: references

4. CONCLUSION

A partial nitridation occurred with a small ZnO incorporation. In addition to the crystalline Ga-oxynitride phase, the presence of amorphous Ga_2O_3 is very likely. Chloride type precursor was found less favorable than the nitrate. Further task is to increase the Zn content and the crystallization degree by the optimization of concentrations and heat treatments.

ACKNOWLEDGEMENT

This project has been supported by the National Development Agency, grant No. KTIA_AIK_12-1-2012-0014. Financial support by the OTKA-project K77720 (András Tompos) is greatly acknowledged.

REFERENCES

Maeda K, Teramura K, Takata T, Hara M, Saito N, et al (2005): J. Phys. Chem. B, 109, 20504-20510.
Maeda K, Domen K (2010): Chem. Matter, 22, 612-623.