РАДІОФІЗИКА

РАДИОФИЗИКА

RADIOPHYSICS

Gorbenko V. I.[1], Gorban A. N.[2]

[1]Ph.D. in physics, associate professor, Classical Private University
[2]D.Sc. in physics, professor, first vice-rector, Classical Private University

THERMAL DECOMPOSITION OF INDIUM PHOSPHIDE IN VACUUM AND ATOMIC HYDROGEN ENVIRONMENT

The thermal decomposition of indium phosphide has been investigated by Auger-electron spectroscopy and mass-spectroscopy. Scanning electron microscopy has been used for study of indium islands growth on surface of the compound semiconductor. The role of atomic hydrogen in processes of decomposition and growth of metallic islands was determined by comparing with these processes under vacuum.

Key words: indium phosphide, atomic hydrogen, thermal decomposition, scanning electron microscopy.

INTRODUCTION

It is now well established that the interaction of atomic hydrogen with clean InP surface leads to a decomposition of the substrate [1–3]. There are two successive stages of the interaction. During first interaction stage H-atoms binds covalently to the substrate and saturates surface unit cells [1, 4]. The second interaction stage leads to a decomposition of the substrate [2]. Auger Electron Spectroscopy (AES) measurements have shown that the ratio of the intensities of the P(120eV) and In(410eV) peaks decrease during the exposure of indium phosphide in atomic hydrogen. The confirmation of a metal presence on the surface was given by Photoemission Yield Spectroscopy (PYS), too. The adsorption stage of the interaction and the decomposition stage are contiguous at doses of hydrogen exposition about 5×10^3–10^4 L. In accordance with estimations in [1] the number of hydrogen atoms reaching the sample during an exposition 10^4 L is 10^{15} atoms/cm^2. The techniques based on high frequency discharge in wet hydrogen allows to obtain 10^{14}–10^{15} H-atoms per cm^3 and its flow to sample surface about 10^{19}–10^{20} atoms$\times$s$^{-1}\times$cm^{-2}

The aim of this report is to present the investigation results of influence of high concentration of atomic hydrogen on the decomposition and the metallization process of indium phosphide.

EXPERIMENTAL

The vacuum equipment and experimental conditions have been described in details elsewhere[5]. We recall that the exposions of InP samples have been carried out in a specially designed vacuum chamber (reactor). To this chamber via diaphragm the monopole mass spectrometer MX7304A (produced by «SELMI», Ukraine) was connected. Such construction gives an opportunity to record a real-time mass spectra of the gas components. The wet hydrogen fed a discharge vessel, which was connected to the reactor. The hydrogen was excited by high-frequency discharge. During experiments the normal working pressure of gases in the reactor was at the level of 10…25 Pa and a base pressure in the spectrometer chamber was of about 10^{-5} Pa. The maximal concentration of atomic hydrogen was at the level of 10^{15} cm^{-3}.

The samples were cut from n-type InP single crystals ($n=1,1\times10^{17}$ cm^{-3} (111)). The standard surface preparations before exposition to the gas mixture in reactor were chemical polishing in a bromine-methanol etchant and successive rinsing in bidistilled and deionised water. During exposition the distance between the discharge and semiconductor sample was about 20 cm that produced conditions for termalization and deionization of gas particles moving from the discharge to the sample.

RESULT AND DISCUSSION

Decomposition. The effect of the high-intensity flow of hydrogen atoms on the decomposition of indium phosphide has been investigated by mass spectrometric method.

The experiments showed that the heating of InP surface up to 800K in hydrogen environment without discharge did

not change the composition of the system gas phase. At higher temperature the diphosphorus molecules were detected. None of the gas hydrogen-phosphorus species were discovered up to 1000 K.

The dependence of diphosphorus partial pressure as function of temperature was similar to that observed during a dissociation of indium phosphide in vacuum. The dependence depicted as Arrenius plots is shown on fig.1 curve (a). From the slope of the curve (a) we have found that the enthalpy of reaction $InP_{(sol)} \rightarrow In_{(sol)} + 1/2P_{2(gas)}$ at 298 K is about 36,9 kcal/mole. It is close to the standard value for this reaction [6]. Probably, the decomposition of indium phosphide in such system is caused by a simple dissociation of the compound.

The exciting of hydrogen by high-frequency discharge added the atomic hydrogen to the system. The exposition of indium phosphide at maximum concentration of the atomic hydrogen caused a drastic change of the process of indium phosphide decomposition. The temperature of the beginning of the decomposition was lower than that for vacuum or molecular hydrogen medium. In our experiments this temperature for both vacuum and unexciting hydrogen was close to 800K and it was reduced by 230 K in the presence of atomic hydrogen. Moreover, in mass spectra both the phosphine and the diphosphorus were observed simultaneously. It is really nothing new to find the PH$_3$ molecules in the systems similar to H/InP. But an appearance of diphosphorus in gas phase at such a low temperature as 570 K was detected for the first time. Finally, the figure 1(b) shows the dependence of diphosphorus partial pressure in the system with atomic hydrogen. Both a shift of the curve to low temperatures and a change of the curve slope are evident. In this case the enthalpy of reaction $InP_{(sol)} \rightarrow In_{(sol)} + 1/2P_{2(gas)}$ at 298K was estimated as 9,32 kcal/mole that is strongly differed from the standard value.

It has been experimentally established that during thermal dissociation of indium phosphide the P_2 and P_4 species are initially forming because they are thermodynamic preferable and P-atoms have enough high surface diffusivity [6]. For treatments of InP with atomic hydrogen HREELS measurements have shown the binding covalently of atomic hydrogen to both P-atom and In-atom on the surface [3, 4]. The saturation of surface by atomic hydrogen leads to a breaking of the bonds between In and neighbouring P-atoms. Probably such interaction of atomic hydrogen with surface atoms is able to cause a releasing of phosphorus atoms similar to a thermal treatment in vacuum. We are thinking that the weakening of In-P bonds by hydrogen interaction with surface is a reason of decreasing both a temperature of InP decomposition and an enthalpy of InP dissociation reaction.

Growth of Indium Islands. The influence of hydrogen atoms on the process of the indium islands growth has been investigated by a comparing with In-islands growth during InP dissociation in vacuum. The scanning electron microscopy method has been used.

The fig. 2 shows the main features of InP surface (111) after the dissociation in vacuum: hexahedral shaped indium islands (label 1); a simple drop with a spherical form (label 2); a drop which has been formed from hexahedral islands (label 3); and the label 4 marks a hexahedral area which was emptied after transition of an indium island from hexahedral to sphere-like shape. On surface of some samples the islands with triangular shape have been observed too. Probably the growth on the (111) surface of triangular and hexahedral islands is conditioned by dislocations of the semiconductor crystal. At a dislocation core the atoms are weaker bound than atoms in the crystal. Therefore the phosphorus atoms of the dislocation core are able to desorb at the lowest temperature that causes an initial nucleation of indium islands at dislocation. That explains a forming of shapes of the islands similar to shapes of etching pits.

Different from that the decomposition of indium phosphide in hydrogen with high concentration of atomic component leads to a forming only spherical islands (fig. 3, *a–d*).
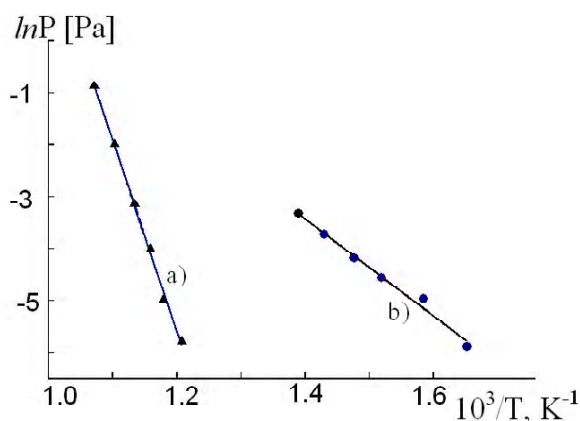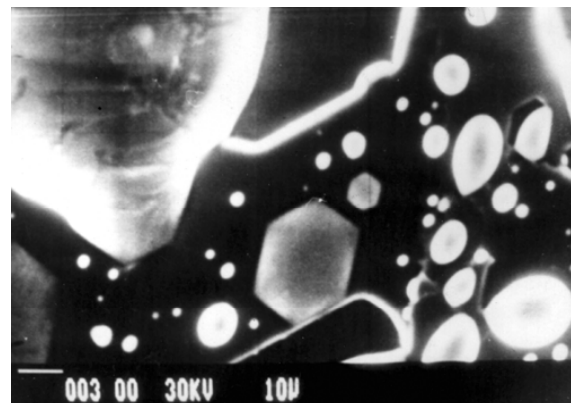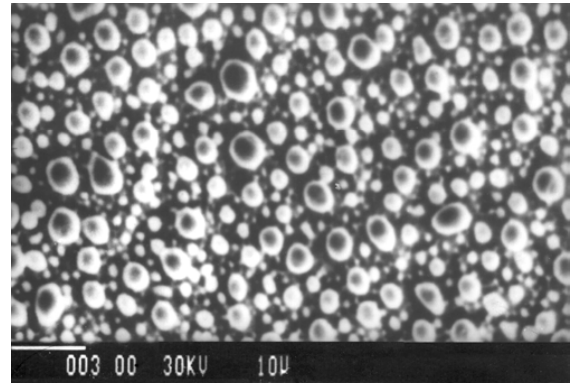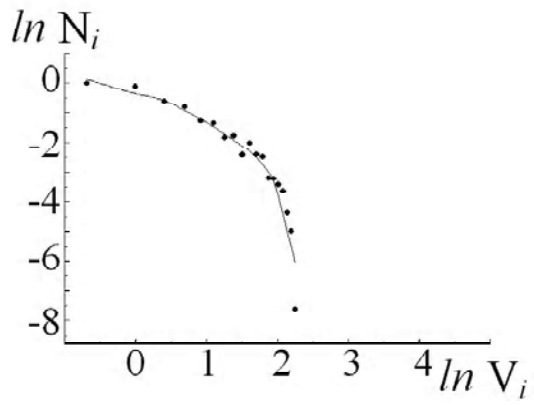

Fig. 1. Dependence of diphosphorus partial pressure as function of temperature:

a) during InP dissociation in vacuum or molecular hydrogen;
b) during InP exposition in hydrogen environment with concentration of H-atoms about 10^{15} cm^{-3}
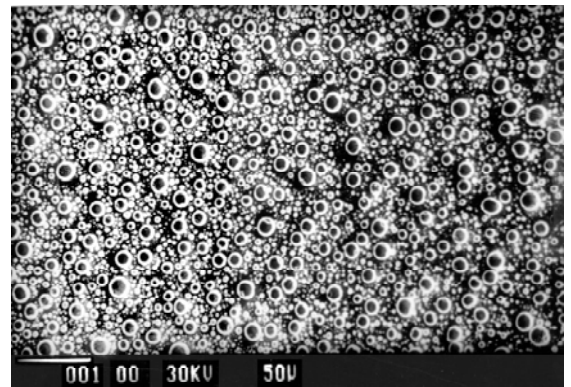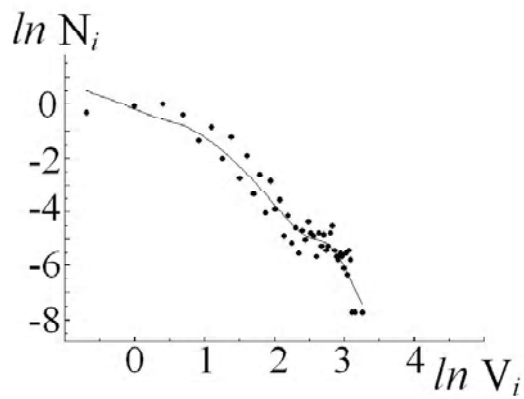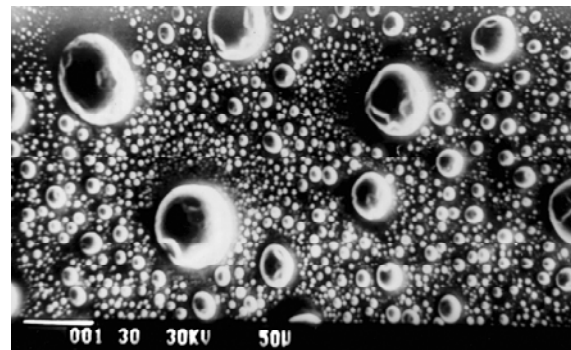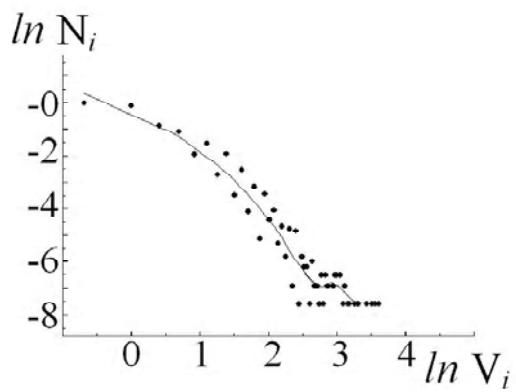

Fig. 2. InP (111) surface after dissociation in vacuum. The temperature of treatment is about 800 K
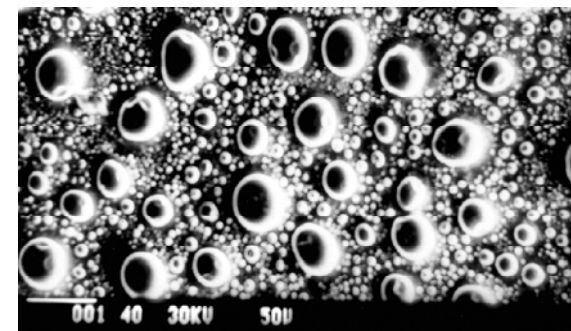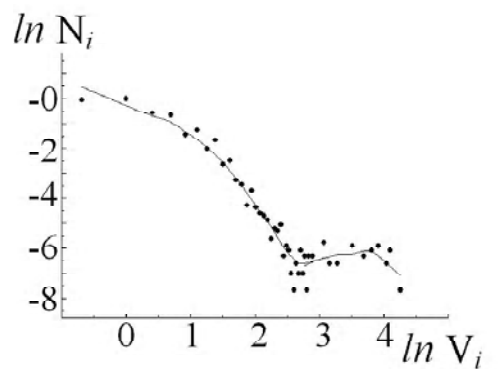
a)

b)

c)

d)

Fig. 3. InP (111) surface after exposition in atomic hydrogen. At left from them the experimental islands size distributions are shown with correspondence to micrographs

Never on such samples the straight-sided islands have not been observed. It is clear that the dislocations do not play a visible role in the process of an interaction of H-atoms with InP surface. The micrographs on fig. 3 are highlighting steps of islands evolution during atomic hydrogen exposition of InP sample.

The first step is incubation not shown on micrographs here. The step duration is depended on temperature of sample and environment. The incubation step comes to an end by formation of small indium drops (for example fig. 3, *a*). At high density of atomic hydrogen flow to a surface the beginning of islands appearance is very difficult to determine exactly. On the left from fig. 3, *a* the typical distribution of islands sizes at start of growth is shown. The sizes of islands form a short range with clear restriction on the right.

The subsequent InP expositions in atomic hydrogen are leading to a spreading of this restriction. Some casual chosen islands grow much faster others. On the distribution in the range of greatest sizes there is a small group which is gradually separating from its basic part. As well as in a case of InP dissociation in vacuum a coalescence is one of the reasons of appearance of large islands. The other reason is non-uniformity of a flow of hydrogen atoms to various areas of a surface. The homogeneity of H-atoms flow is upsetting after forming of metal subsystem on the sample surface. Really the metallic islands catalyse the recombination reaction of hydrogen atoms to molecule. Therefore the forming of indium islands leads to increasing of gradient of the atomic hydrogen concentration near to the sample surface. During recombination act the energy about 4,3 eV is produced. With a combination of an intensive flow of H-atoms it can give the additional heating of islands and cause the enhancing process of decomposition. Really the metallic islands catalyze the recombination reaction of hydrogen atoms to molecule. Therefore the forming of indium islands leads to increasing of gradient of the atomic hydrogen concentration near to the sample surface. During recombination act the energy about 4,3 eV is produced. With a combination of an intensive flow of H-atoms it can give the additional heating of islands and cause the enhancing process of decomposition. Any island that has larger size than nearest neighbours is able to change the gradient of H-atoms concentration and more intensive flow of H-atoms is forming to this island. It is clear such island grows faster than its neighbours at the same time the growth of neighbours is depressed more and more. Fig. 3 *c*, *d* and enclosed distributions illustrate such behavior of islands.

CONCLUSION

The role of atomic hydrogen in the processes of indium phosphide decomposition and growth of indium islands on InP(111) surface has been studied. The increasing of concentration of atomic hydrogen in gas phase causes a decreasing of minimal temperature of the indium phosphide decomposition. During decomposition the species P_2, P_4 and PH_3 are forming. The enthalpy of reaction $InP_{(sol)} \rightarrow In_{(sol)} + 1/2 P_{2(gas)}$ is strongly decreased in the presence of atomic hydrogen. The catalytic properties of indium to the reaction of recombination of hydrogen atoms are influencing on process of island growth. The steps of island evolution during atomic hydrogen exposition of InP sample have been established.

REFERENCES

1. *M'hamedi, O.* Interaction of atomic hydrogen with cleaved InP. I. The adsorption stage / M'hamedi O., Proix F., Sebenne C. A. // Journal of Vacuum Science and Technology A. – 1988. – Vol. 6, № 2. – P. 193–198.
2. *Proix, F.* Interaction of atomic hydrogen with cleaved InP. II. The decomposition stage / Proix F., M'hamedi O., Sebenne C. A. // Journal of Vacuum Science and Technology A. – 1988.– Vol. 6, № 2. – P. 199–203.
3. *Proix, F.* Dissociation effects of H and H_2^+ on clean III–V compounds / Proix F. // Physica B. – 1991. – № 170. – P. 457–468.
4. *Schaefer, J. A.* Atomic hydrogen – a local probe for interface characterization / Schaefer J. A. // Surface Science. – 1987. – № 189/190. – P. 127–136.
5. *Gorbenko, V.* Oxidation and metallization in $H_2/H_2O/InP$ system / Gorbenko V., Shvets J., and Gorban A. // Proceedings of the Twenty-Seventh State-of-The-Art Program On Compound Semiconductors (SOTAPOCS XXVII) by editors S. N. G.Chu, D. N. Buckley, K. Wada et. al. Vol. 97 21. – The Electrochemical Society, Pennington, 1997. – P. 375–381.
6. *Panish, M. B.* Phase equilibria and vapor pressures of the system In+P / Panish M. B., Arthur J. R. // J. Chem. Thermodynamics. – 1970. – vol. 2, № 3. – P. 299–318.

Горбенко В. И., Горбань А. Н.
ТЕРМИЧЕСКАЯ ДЕКОМПОЗИЦИЯ ФОСФИДА ИНДИЯ В ВАКУУМЕ И В СРЕДЕ С АТОМАРНЫМ ВОДОРОДОМ

Исследование термической декомпозиции фосфида индия и изменения морфологии поверхности выполнено при помощи Оже-электронной спектроскопии, масс-спектроскопии и сканирующего электронного микроскопа. Влияние атомарного водорода на процесс декомпозиции фосфида индия, возникновение и рост островков индия определено благодаря сравнению с подобными процессами в условиях вакуума.

Ключевые слова: фосфид индия, атомарный водород, термическая декомпозиция, сканирующая электронная микроскопия.

Горбенко В. І., Горбань О. М.
ТЕРМІЧНА ДЕКОМПОЗИЦІЯ ФОСФІДУ ІНДІЮ У ВАКУУМІ ТА В СЕРЕДОВИЩІ З АТОМАРНИМ ВОДНЕМ

Термічна декомпозиція фосфіду індію у вакуумі та в середовищі з атомарним воднем

Дослідження термічної декомпозиції фосфіду індію та морфологічних змін поверхні проводилось за допомогою Оже-електронної спектроскопії, масс-спектроскопії та скануючого електронного мікроскопа. Вплив атомарного водню на процес декомпозиції фосфіду індію, виникнення та ріст індієвих островків визначено завдяки порівнянню з подібними процесами в умовах вакууму.

Ключові слова: фосфід індію, атомарний водень, термічна декомпозиція, скануюча електрона мікроскопія.