| Cryst. Res. Technol. | 35 | 2000 | 6–7 | 745–749 |
|---|---|---|---|---|

S. A. NEPIJKO*, M. KLIMENKOV**, H. KUHLENBECK, H.-J. FREUND

Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany
* also Institute of Physics, National Academy of Sciences of Ukraine, Kiev, C.I.S./Ukraine
** also Institute of Ion Beam Physics and Materials Research, Research Center Rossendorf, Dresden, Germany

# Local Melting of the NiAl Substrate Under Deposited Pd Clusters During Irradiation in a Transmission Electron Microscope

*Dedicated to Prof. Dr. J. Heydenreich on the occasion of his 70th birthday*

The holes with diameters in the nanometer range was created in the $Al_2O_3$/NiAl(110) substrate if metal clusters deposited on it are irradiated by the intense convergent electron beam in a transmission electron microscope. The localisation and size of holes can be controlled to some extent. The formation of holes can be interrupted by lowering the beam intensity below a critical value. It can be continued by increasing the intensity above the threshold value. We have also disclosed the necessity of clusters' presence on the surface for the start of holes' formation. It was shown earlier that holes thus created are characterized the perfect crystallographic faceting. The method for producing a single nanohole has been described in the present paper.

Keywords: Pd cluster, Moiré pattern, local melting, high-resolution transmission electron microscopy (HREM), converted beam electron diffraction (CBED)

(Received May 3, 2000; Accepted July 1, 2000)

## Introduction

Investigation of a system consisting of Pt clusters on $\gamma$-$Al_2O_3$/NiAl(110) has shown that holes are created under clusters as a result of irradiation of this system by the electron beam of sufficiently high intensity [NEPIJKO 1999-1]. This effect can play a positive or negative role, but it deserves further investigation. It is of interest whether this phenomenon has a general character or not. Mechanism of hole creation, its locality and a possible practical implementation of this effect can be interesting as well. The present study was undertaken to answer these questions.

The system including Pd clusters on $\gamma$-$Al_2O_3$/NiAl(110) was investigated. This system is the most similar to the one studied earlier [NEPIJKO 1999-1], but it has a principal distinction. Pd is really just above Pt in the periodic table, i.e. they have the same configuration of outer electron shells. These noble metals are only slightly oxidizable. If some reactions do occur under the action of electron beams, they are of the same type. A principal distinction lies in the fact that epitaxial clusters of Pt and Pd grow on $\gamma$-$Al_2O_3$/NiAl(110) substrate as two-dimensional [LIBUDA] or three-dimensional ones [BÄUMER], respectively. Moreover in the literature exists several descriptions of cluster systems from both this metals on $\gamma$-$Al_2O_3$/NiAl(110) [BÄUMER; KLIMENKOV 1997-1; LIBUDA; NEPIJKO 1999-2]. The knowing of the cluster behaviour during their growth, their density, the size distribution enables the obvious interpretation of the results.

To study locality of the hole formation in a substrate under a metal cluster, this cluster was irradiated by the convergent electron beam having size less than mean distances between clusters. The goal was to find out the conditions of creation of nanosized holes with a controllable diameter in a given place.

## Experimental

A cone-shaped hole was made by ion etching at an small angle in the [110] oriented disk-like NiAl single crystal 3 mm in diameter and 0.1 mm thick. The further preparation of such a specimen included preparation of an atomically clean well-ordered surface of NiAl(110), production an epitaxial $\gamma$-$Al_2O_3$(111) layer 0.5 nm thick and epitaxial growth of Pd clusters. This was made in the same ultra-high vacuum (UHV) unit ($2\cdot10^{-10}$ mbar) and is described in detail in [BÄUMER; LIBUDA; NEPIJKO 1999-1 and -2]. Three-dimensional Pd clusters thus formed [BÄUMER] are characterized by the following orientation: Pd cluster (111)||$\gamma$-$Al_2O_3$(111)||NiAl(110) [NEPIJKO 1999-2].

The further investigation was performed in the microscope Philips CM-200 FEG using regime of the high-resolution transmission electron microscopy (HRTEM) and the microbeam operation mode. The accelerating voltage and the ultimate resolution were 200 kV and 0.144 nm, respectively. The convergent electron beam enabled to an irradiated region size to be diminished down to 10 nm at the current density of 200 A/$cm^2$. The substrate thickness was determined by means of the converted beam electron diffraction (CBED).

Pd films were prepared with the concentration of clusters which did not exceed $10^{12}$ $cm^{-2}$. In this case clusters were arranged on the substrate surface in such a way that distances between them were more than 10 nm. Then the convergent electron beam could act only on a single chosen cluster as shown in a scheme in fig.1.

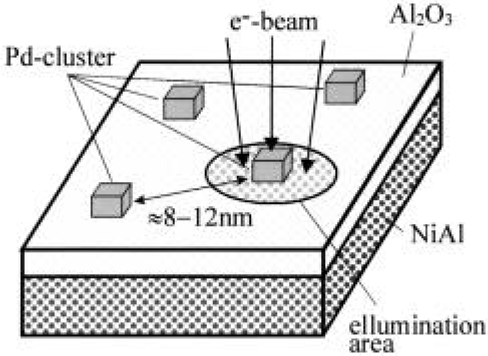


Fig. 1: A scheme of the experimental arrangement.

## Experimental results and discussions

Fig.2*a* shows an electron-microscopic photograph of the system being investigated. It was taken with high resolution. The fringes of atomic planes of (001) NiAl with distance between them equal to 0.278 nm and several systems of the Moiré fringes are seen there. The Moiré fringes are formed as a result of the double electron diffraction on the crystal lattices of NiAl and $\gamma$-$Al_2O_3$ [KLIMENKOV 1997-1] as well as on the crystal lattices of NiAl and Pd [NEPIJKO 1999-2]. It is always possible to find out from the distance between the Moiré fringes whether the second lattice belongs to $\gamma$-$Al_2O_3$ or to Pd. In particular, the Moiré pattern from Pd cluster is set off by a circle in fig.2. The image of Pd clusters is characterized by a low contrast. The conditions of their observation with high resolution are described in [NEPIJKO 1999-2]. They can be well visualized in the dark-field operation mode.

The convergent electron beam with the current density of 100-200 A/cm$^2$ was focused on the region denoted by the circle in fig.2. This current density value is sufficient for the formation of a hole. Area irradiated by electrons has a linear size near 10 nm as illustrated schematically in fig.1. The small beam size arises the possibility to produce a hole in the substrate only under a chosen cluster. After each exposure under the electron beam during 30 s, the microscope was adjusted in the usual HRTEM mode in order to enable taking micrographs. The adjustment procedure takes about 100 s. During this time the current density was lowered down to 0.05 A/cm$^2$ to avoid uncontrolled changes of the sample. The substrate thickness in this region was determined by means of the CBED and comprised about 60 nm.

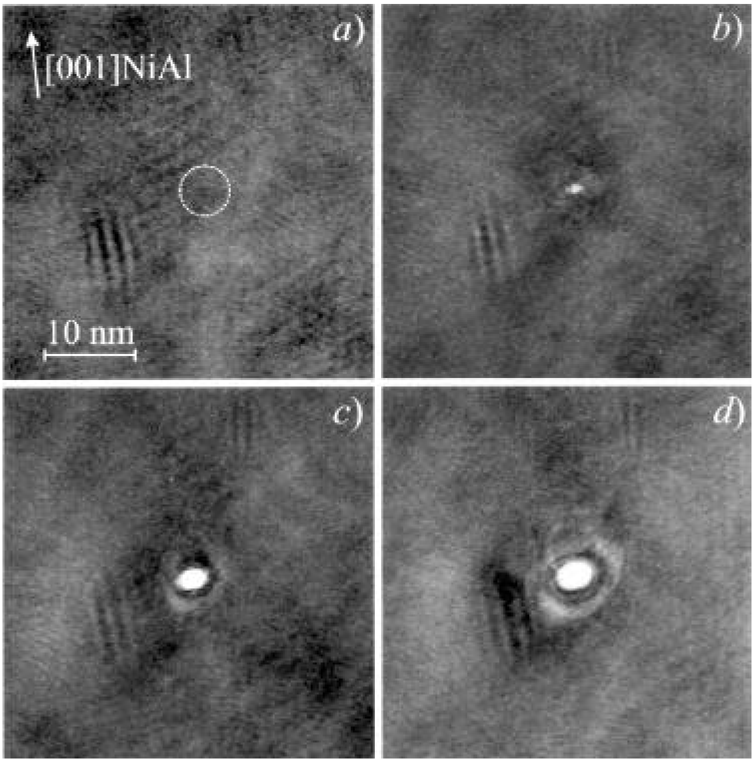


Fig. 2: Hole formation in the substrate. The circle shows the electron-irradiated area with exposition time of $t$ = 0 (*a*), 30 (*b*), 60 (*c*) and 90 s (*d*).

The temperature of metal clusters under electron irradiation can significantly exceed the substrate temperature [GRYAZNOV]. Therefore, it was proposed in [NEPIJKO 1999-1] that holes are created due to a local temperature increase. In order to better understand the mechanism of hole creation, it is necessary to study the thermal field in substrate. There are publications devoted to definition of the substrate temperature under action of the electron beam [GALE; GRYAZNOV; REIMER 1965; STENN; WILLIAMS]. Analysis of these articles is given in the book written by Reimer (1993). He shows that precise temperature definition is possible only in systems with very simple boundary conditions. It is especially difficult to determine the temperature distribution when it becomes as high as 1200 K and higher because in this case losses due to the temperature radiation can not be neglected. Our system is rather complicated and exact determination of the thermal field of a wedge-shaped sample presents difficulties. Estimation of the thermal flow between a particle and this substrate is impossible at all. So, we do not present the theoretical calculations here and give only quality estimation of some conditions necessary for creation of such a hole.

Experimental results shown in fig.2*a-d* demonstrate creation of a hole 4 nm in diameter and 60 nm in depth. The cluster is marked on the micrograph before irradiation with a circle (fig. 2a). The Moiré fringes indicate the presence of epitaxial grown 2 nm cluster. The cluster and fringes have a weak contrast because of the "heavy" NiAl support. It is typically that $\gamma$-$Al_2O_3$ layer is destroyed only just close to a cluster. As illustrated in fig.2*d*, Moiré fringes, formed as a result of the double electron diffraction on the crystal lattices of $\gamma$-$Al_2O_3$ and NiAl(110), are observed at the distance of 8 nm from the hole. It means that at this distance the substrate temperature did not exceed the temperature of 1200 K higher which $\gamma$-$Al_2O_3$ decomposes [KLIMENKOV 1997-2]. Sharp edges of hole (fig. 2*d*) indicated that there is a strong temperature gradient. In the place of hole creation temperature did reach or even exceeded somewhat the melting temperature of NiAl ( $T_m^{(NiAl)}$ = 1911 K), but at the distance of 2 nm from this place temperature was lower then the substrate melting temperature $T < T_m^{(NiAl)}$. Let us take the temperature difference equal to 1 K. Then the thermal flux through the surface *S* around a hole (lateral surface of a hole) is given by

$$P = -l\,S\Delta T\ , \qquad (1)$$

where $l$ is the coefficient of thermal conductivity of NiAl, $\Delta T$ is the temperature gradient. If there are not any clusters, the electron beam energy is absorbed throughout the specimen width. Then power, transmitted through the lateral walls of hole, comprises $4{\cdot}10^{-5}$ W. This value is comparable with the whole power of the electron beam which is equal to $3.14{\cdot}10^{-5}$ W at the current density 200 A/cm$^2$, 200 keV energy and 10 nm beam diameter. Hence it follows that it is impossible to create a hole of this kind in a homogeneous system. A strong temperature gradient is necessary to form a hole, and it should be gradient only between a cluster and a substrate. It means that existence of metal clusters on the substrate surface is a condition necessary for creation of holes in this substrate. The open question remains why the holes size increase after complete formation.

We suppose that Pd cluster is heated under the electron beam up to a higher temperature than the melting temperature of NiAl substrate. The substrate just in the region of its contact with Pd cluster is heated up to this temperature. Since the metal substrate withdraws heat very well, its temperature decreases rapidly as the distance from the Pd cluster increases. As a result, a substrate is melted only under the Pd cluster. Then the hole edges have the regular crystal faceted shape (fig. 2*d*, see also [NEPIJKO 1999-1]). The hole formation in NiAl requires the current densities of about 100-200 A/cm$^2$. This value is approximately the same as in the experiment with platinum cluster [NEPIJKO 1999-1]. The difference between melting temperatures of both metals $T_m^{(Pt)}$ = 2042 K and $T_m^{(Pd)}$ = 1825 K doesn't have a significant influence on the process.

## Conclusion

The performed investigation has shown that holes in $\gamma$-$Al_2O_3$/NiAl substrate are formed under two-dimensional metal clusters as well as under three-dimensional ones when the electron beam with sufficiently high intensity irradiates this system. The sizes of formed holes fall in the nano-sized range. They rise as the radiation dose increases.

The fulfilled theoretical estimations indicate that the creation of holes is not caused by dissipation of electron energy by the NiAl support. The experimental data suggest that presence of metal clusters on the surface is the necessary condition for creation of nanoholes in NiAl substrate.

The phenomena being investigated can be used in practice, for example, to produce nanomembranes or diaphragms with nanoholes. In the latter case, a homogeneous system of metal clusters is prepared on the surface of $\gamma$-$Al_2O_3$/NiAl. It is always possible to find a cluster close to a point where a hole should be made with the accuracy of typical distances between clusters. Then the chosen cluster should be irradiated by the convergent electron beam, and, as a result of its action, a nanohole is created in the substrate at this place.

*Acknowledgements*

The authors thank the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen (Referat IV A5, D. Dzwonnek) and the Deutsche Forschungsgemeinschaft for financial support of our work witch was partly carried out within the framework of the “Forschergruppe Modellkat”.

## References

BÄUMER M., LIBUDA J., SANDELL A., FREUND H.-J., GRAW G., BERTRAMS TH., NEDDERMEYER H.: Ber. Bunsenges. Phys. Chem., **99** (1995) 1381.
GALE B., HALE K.F.: Br. J. Appl. Phys., **12** (1961) 115.
GRYAZNOV V.G., KAPRELOV A.M., BELOV A.Y.: Phil. Mag. Lett., **63** (1991) 275.
KLIMENKOV M., NEPIJKO S., KUHLENBECK H., FREUND H.-J.: Surf. Sci., **385** (1997) 66.
KLIMENKOV M., NEPIJKO S., KUHLENBECK H., BÄUMER M., SCHLÖGL R., FREUND H.-J.: Surf. Sci., **391** (1997) 27.
LIBUDA J., BÄUMER M., FREUND H.-J.: J. Vac. Sci. & Technol. A, **12** (1994) 1.
NEPIJKO S.A., KLIMENKOV M., KUHLENBECK H., FREUND H.-J.: J. Vac. Sci. & Technol. A, **17** (1999) 577.
NEPIJKO S.A., KLIMENKOV M., ADELT M., KUHLENBECK H., FREUND H.-J.: Langmuir, **15** (1999) 5309.
REIMER L., CHRISTENHUSZ R.: Lab. Invest., **14** (1965) 1158.
REIMER L.: Transmission electron microscopy. Physics of Image Formation and Microanalysis, Ed. P. W. Hawkes, Springer Series in Optical Sciences, vol.36, Springer-Verlag, Berlin-Heidelberg-New York-Barcelona-Budapest-Hong Kong-London-Milan-Paris-Santa Clara-Singapore-Tokyo 1993.
STENN K., BAHR G.F.: J. Ultrastruct. Res., **31** (1970) 526.
WILLIAMS P.: Appl. Phys. Lett., **50** (1987) 1760.

*Contact information:*

S. A. NEPIJKO*
Institute of Physics of the National Academy of Sciences of Ukraine
Prospekt Nauki 46
03650 Kiev, C.I.S./Ukraine

M. KLIMENKOV
Research Center Rossendorf
PO Box 51 01 19
01314 Dresden, Germany

H. KUHLENBECK, H.-J. FREUND
Fritz-Haber-Institute of the Max-Planck-Society
Faradayweg 4-6
14195 Berlin

*corresponding author
e-mail: nepijko@yahoo.com