

Growth and Structural Evolution of Nanosized Ni on (001) MgO by *in situ* TEM

H.P. Sun*, W. Tian*, Y.B. Chen*, J.H. Yu**, M. Yeadon**, C.B. Boothroyd**, R.A. Lukaszew***, R. Clarke****, and X.Q. Pan*

*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

**Institute of Materials Research and Engineering, Singapore, 117602

***Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606

****Department of Physics, The University of Michigan, Ann Arbor, MI 48109

Nucleation and growth of metal particles on oxide surface is of theoretical and practical interest. Ni film has been grown on MgO [1], but its growth behavior at early stage has never been studied. In the present work, the nucleation and growth of epitaxial nanosized Ni particles on MgO (001) surface was investigated by *in situ* transmission electron microscopy (TEM). A hexagonal close-packed (hcp) structure of element Ni was discovered and its subsequent transition to face centered cubic (fcc) structure was observed.[2]

Ni was deposited on the MgO (001) surface in a modified JEOL-2010 TEM which is dedicated for *in-situ* deposition under ultra-high vacuum (UHV) conditions. Atomic Ni flux was generated by the electron beam evaporation of high purity Ni metal. Electron transparent (001) MgO substrates were prepared with smooth surface. The structural evolution of Ni particles during the deposition was monitored *in situ*.

Figure 1 shows the morphology and structure evolution of Ni grown on MgO (001). It is clear that the growth is in the form of three dimensional islands. At the early stage of the growth (Fig.1a), electron diffraction pattern (Fig.2a) revealed that the crystal structure of the epitaxial Ni islands is hcp. The hcp phase of Ni does not exist in nature and is thought to be stabilized by epitaxy. The primary orientation relationship between the *hcp*-Ni islands and the MgO substrate is $(1\bar{1}20)\langle 0001\rangle\text{Ni}_{\text{hcp}}//\langle 001\rangle\langle 100\rangle\text{MgO}$. Two orthogonal growth variants are expected to occur on the (001) MgO surface, namely $[0001]\text{Ni}//[100]\text{MgO}$ and $[0001]\text{Ni}//[010]\text{MgO}$. The hcp Ni islands subsequently transform into the normal fcc structure with fcc Ni $(110)//\text{MgO}(001)$ when the lateral size of the islands exceeds a critical value of $\sim 5\text{nm}$ (Fig.1b). Corresponding electron diffraction pattern is shown in Fig.2b. There are four different in-plane orientations of the $[110]$ Ni islands. As deposition proceeds, the $[110]$ oriented fcc Ni islands will change into the $[001]$ orientations with an orientation relationship of $(001)[100]_{\text{fcc-Ni}}//\langle 001\rangle[100]\text{MgO}$ (Fig.2c,d).

In conclusion, we found a highly strained hcp form of Ni which is stabilized by heteroepitaxial growth on the (001) face of MgO. The hcp phase of nickel is stabilized by the strong coherent covalent bonding between Ni atoms and O atoms in MgO at the interface, through a pseudomorphic growth mechanism. The driving force for the hcp to fcc transformation is the reduction of lattice energy in the Ni islands. The structural transition proceeds via a Martensitic change in the stacking sequence of the close-packed planes, representing a novel way to relieve misfit strain.

References:

[1] A. Barbier et al. J. Appl. Phys. 84 (1998) 4259.

[2] W. Tian, et al., submitted to Phys. Rev. Lett.

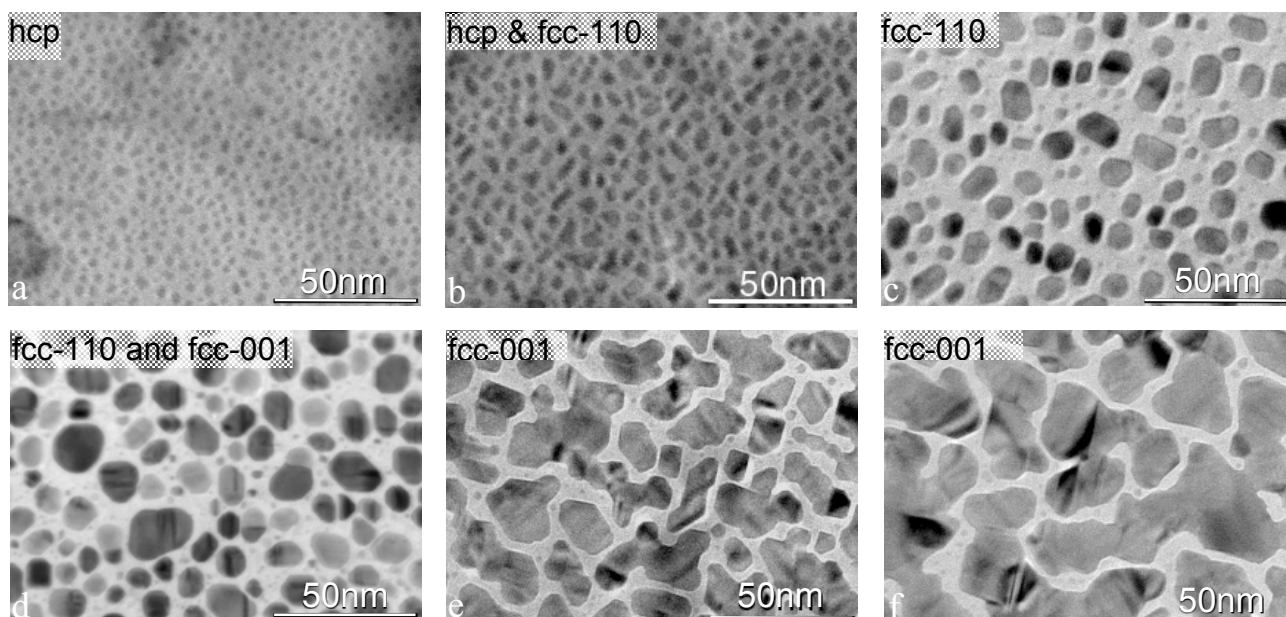


FIG. 1. Time series TEM images showing the morphology of epitaxial Ni islands on MgO (001) surface deposited *in situ* in TEM with increasing deposition time from (a) to (f). The labels indicate the dominate phase of Ni for corresponding image.

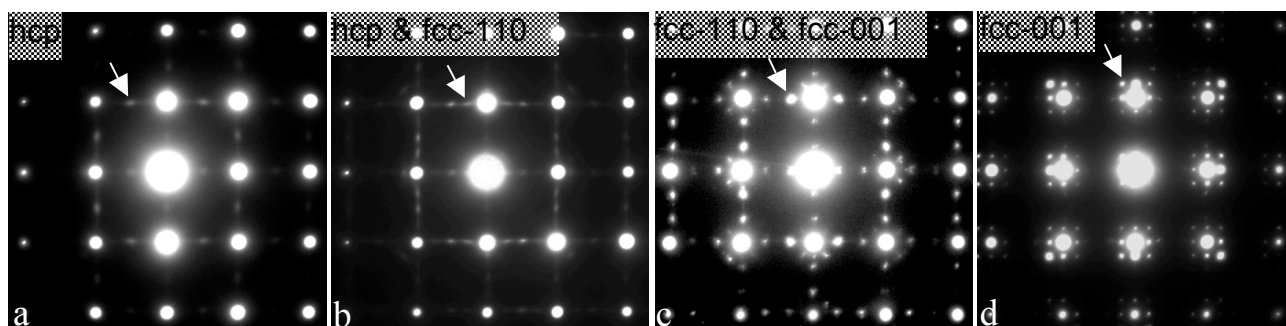


FIG. 2. Time series electron diffraction patterns of Ni on MgO (001) surface with increasing deposition time from (a) to (d). The strong spots in each pattern are reflections from MgO. The arrow in (a) indicates the reflection from hcp-Ni. The arrows in (b) and (c) indicate the reflections from fcc-Ni with (110) orientation. The arrow in (d) indicates the reflection of fcc-Ni with (001) orientation.