Coadsorption of chlorine and oxygen on Ag(111):

STM and DFT study

Boris V. Andryushechkin, Vladimir M. Shevlyuga, Tatiana V. Pavlova,

Georgy M. Zhidomirov, Konstantin N. Eltsov

A.M.Prokhorov General Physics Institute of Russian Academy of Sciences,
Vavilov str.38, 119991 Moscow, Russia
andrush@kapella.gpi.ru

Adsorption of chlorine and oxygen on silver surface has been a subject of numerous studies since the 1970s. However, a significant progress in the understanding of O/Ag and Cl/Ag systems has been achieved only in the 2000s after the application of scanning tunneling microscopy in a combination with DFT calculations [1-4]. Coadsorption of chlorine and oxygen was studied only in several earlier investigations [5-6].

In this work, we have studied coadsorption of chlorine and oxygen on the Ag(111) surface with LT-STM and DFT. Figure 1 shows a series of STM images obtained at the initial stage of chlorine adsorption onto the Ag(111)-p(4x4)-O surface. Adsorption of chlorine leads to the appearance of new bright objects located between protrusions of the 4x4 reconstruction (Fig.1a). As chlorine adsorbs, objects form "rosettes" around corner holes (Figs.1b,c). This configuration coincides with the configuration of the chlorine atoms in the Ag(111)-(3x3)-Cl reconstruction structure [4] shown in the inset to Fig.1c. We conclude that the adsorption of chlorine on the Ag(111)-p(4x4)-O surface occurs dissociatively, with chlorine atoms displacing oxygen atoms from the four-fold positions. Further chlorination can result in the formation of formation of several mixed phases corresponding to the different Cl/O stoichiometries. Adsorption of oxygen on the Ag(111) surface with preadsorbed chlorine gives rise to the formation of another series of mixed phases. Thus, chlorine and oxygen do not prefer to form separate domains on Ag(111). According to DFT calculations, the atomic structure of the mixed Cl-O phases can be explained by the formation of the Ag_xClO_y configurations.

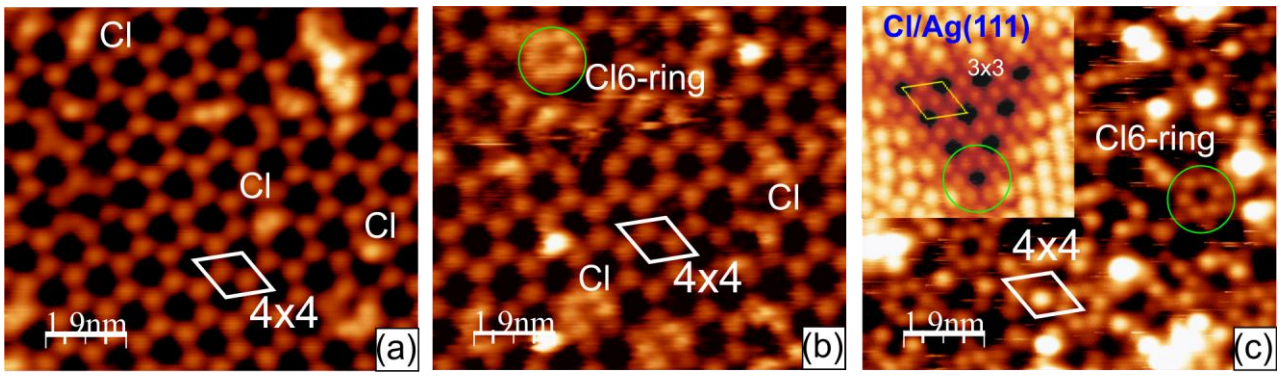

Fig.1 STM images (77 K) of the Ag(111)-p(4x4)-O surface obtained in the course of the step-by-step adsorption of Cl_2 at 300 K.

This work was supported by Grant No. 16-12-10546 of the Russian Science Foundation.

References:

[1] C.I. Carlisle et al., Phys. Rev.Lett. **84**, 3899 (2000).
[2] M.Schmid et al., Phys. Rev.Lett. **96**, 146102 (2006).
[3] J. Schnadt et al., Phys. Rev.Lett. **96**, 146101 (2006).
[4] B.V. Andryushechkin et al, Phys. Rev.B **81**, 205434 (2010); Phys. Rev.B **84**, 075452 (2011).
[5] G. Rovida et al., J. Catal. **41**, 140 (1976).
[6] C.T.Campbell, M.T. Paffett, Appl. Surf. Sci. **19**, 28 (1984).