Effect of defects on reaction of NiO surface with Pb-contained solution

Jongjin Kim1, Binyang Hou2, Changyong Park3, Ji Bum Bahn3, Jason Hoffman1,†, Jennifer Black4, Anand Bhattacharya1, Nina Balke4, Hawoong Hong5, Ji Hyun Kim6 & Seungbum Hong1

In order to understand the role of defects in chemical reactions, we used two types of samples, which are molecular beam epitaxy (MBE) grown NiO(001) film on Mg(001) substrate as the defect free NiO prototype and NiO grown on Ni(110) single crystal as the one with defects. In-situ observations for oxide-liquid interfacial structure and surface morphology were performed for both samples in water and Pb-contained solution using high-resolution X-ray reflectivity and atomic force microscopy. For the MBE grown NiO, no significant changes were detected in the high-resolution X-ray reflectivity data with monotonic increase in roughness. Meanwhile, in the case of native grown NiO on Ni(110), significant changes in both the morphology and atomistic structure at the interface were observed when immersed in water and Pb-contained solution. Our results provide simple and direct experimental evidence of the role of the defects in chemical reaction of oxide surfaces with both water and Pb-contained solution.

Physical and electrical properties of ionic crystals are dominated by the structure and concentration of the defects in many cases1–4. Furthermore, the defects are often responsible for mass transport, which determine materials property for advanced functionalities such as diffusion barriers5 and oxygen ion conductors6. For oxidation/corrosion on the metals, the defects (e.g., vacancies, interstitial atoms, dislocations, grain boundaries) accelerate the reaction process by providing a pathway for fast oxygen diffusion or a favorable place for the reaction to occur7. When metals react with oxygen, they form a solid oxide film or scale on the surface under most conditions. Depending on the oxidation conditions (e.g., temperature, time, pressure, gas composition), the oxide films may have varying microstructures and morphologies, and usually develop microcracks or microchannels8,9.

Many studies were performed to investigate the formation and accumulation of defects on oxide and its effect on the oxidation/corrosion10,11. Localized corrosion such as pitting corrosion has been of particular interest as it is one of the major degradation mechanisms affecting the integrity of materials, which occurs around defects12,13. Meletis and Lian14 proposed the vacancy/dislocation interaction mechanism of transgranular stress corrosion cracking as the subsurface vacancies interact with dislocations promoting their motion and modifying their configurations. Burststein et al.15 reported a mechanism of pitting corrosion, and demonstrated that pit nucleation occurs at preferential sites for some metals. Some impurities such as Pb, Cl and S accelerate the oxidation and corrosion, and although there are a lot of studies on investigation of the corrosion behavior in such impurities16–20 the interaction between impurities and defects remains still elusive if not fully understood.

In case of the nuclear industry, corrosion and cracking of structural materials in nuclear power plants is one of the major issues for plant safety and life extension. In pressurized water reactors (PWRs), a steam generator (SG) consists of thousands of metal tubings made of nickel-base alloys, which suffer from corrosion and stress corrosion cracking (SCC)11,12. Recent laboratory test data indicated that Alloy 690 used for tubing could be susceptible to corrosion and SCC under lead (Pb)-contaminated water and even more susceptible than Alloy 600 especially in high pH solution20. To understand the mechanism, the process of the interaction between Pb contained solution and surface oxide (hydroxide) needs to be observed from the very beginning.

1Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA. 2HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, USA. 3School of Mechanical Engineering, Pusan National University, Busan 46241, Republic of Korea. 4Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. 5Advanced Photon Source, Argonne National Laboratory, Lemont, IL 60439, USA. 6Department of Mechanical Engineering, School of Mechanical and Nuclear Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea. 7Department of Materials Science and Engineering, KAIST, Daejeon 34141, Republic of Korea. †Present address: Department of Physics, Harvard University, Cambridge, MA 02138, USA. Correspondence and requests for materials should be addressed to J.K. (email: 83jjkim2@gmail.com) or S.H. (email: seungbum@kaist.ac.kr)
At this point, we raise a fundamental question of “Can we design a model experiment to investigate the role of defects in the chemical reaction between the oxide surface and Pb contained solution?” We used molecular beam epitaxy (MBE)\textsuperscript{24–26} as a tool to create defect-free NiO thin films on Mg(001) substrate, which can grow high-purity single crystal quality epitaxial films via operating in ultra-high vacuum (UHV) chamber and using high purities of the beam fluxes in the Center for Nanoscale Materials at Argonne National Laboratory. For the oxide films with defects, we used the process of growing polycrystalline NiO thin films on Ni(110) single crystals in UHV chamber reported elsewhere\textsuperscript{27,28}. Using the samples with and without defects, we directly investigated the role of defects in Ni oxide thin films on their chemical reaction in water and Pb-contained solution. High resolution X-ray reflectivity was adopted to measure the interface structure between oxide and water or oxide and Pb-contained solution, and \textit{in-situ} atomic force microscopy were used to investigate the morphology changes of oxide films in water and Pb-contained solution.

**Results and Discussion**

In order to explore the effect of defects in NiO layer on the chemical reaction between NiO layer and water as well as Pb contained solution, we prepared two types of NiO: one is as-grown NiO on Ni(110) substrates where we expect to have defects such as phase boundary, and the other is MBE grown epitaxial NiO on MgO(001), which is relatively free from such (defect-free NiO). The changes in interfacial structure and surface morphology in water and Pb-contained solution were investigated by high resolution X-ray reflectivity (HRXR) and \textit{in-situ} atomic force microscopy (AFM).

Figure 1 shows the measured X-ray reflectivity data from the as-grown NiO on single crystal Ni(110) surface in helium environment and in deionized water, respectively. For the measured reflectivity in helium environment, the reflectivity shows distinct beating patterns at lower $q$ side corresponding to the existence of at least two layers with different densities. However, near the substrate (220) Bragg peak, the regular film fringes appeared along the substrate reflectivity. This is a strong evidence that one of these layers have epitaxial relationship with the substrate, which suggests the existence of a crystalline NiO layer. As the film Bragg peak shows only one epitaxial layer without complicated beating pattern, we think that the other layer is either amorphous or polycrystalline phase\textsuperscript{29}.

On the other hand, the reflectivity measured in deionized water from the identical surface shows completely different features in the intensity distribution compared to that measured in helium environment. For the measured reflectivity in helium environment, the reflectivity shows distinct beating patterns at lower $q$ side corresponding to the existence of at least two layers with different densities. However, near the substrate (220) Bragg peak, the regular film fringes appeared along the substrate reflectivity. This is a strong evidence that one of these layers have epitaxial relationship with the substrate, which suggests the existence of a crystalline NiO layer. As the film Bragg peak shows only one epitaxial layer without complicated beating pattern, we think that the other layer is either amorphous or polycrystalline phase\textsuperscript{29}.

Two possibilities are suggested for these observations: one is that the as-grown NiO layer, regardless of its phase, interacts with water to be dissolved and the metal surface starts to form nickel hydroxide ad-layers whereas the other is that the intense X-ray generates reactive radicals in water nearby the oxide surface and causes secondary beam damage effects (e.g., continuous etching of the bare surface as well as oxide dissolution)\textsuperscript{31,32}. We conducted an experiment to explore the X-ray beam damage effect, which will be discussed in the latter part of our discussion. It should be noted that we were not able to measure the X-ray reflectivity in Pb contained solution due to the disappearance of surface crystallinity when the sample was in contact with water.

Figure 2 shows the X-ray reflectivity results of MBE grown nickel oxide on MgO substrate in helium, deionized water and 10 mM Pb-contained solution, respectively. The red boxes show the magnified images of the reflectivity close to the right shoulder of each Bragg peak. Commonly for all three cases, at the MgO(002) substrate Bragg peak, the film fringes at the left and right sides of the Bragg peak show slightly different features, of which difference is more prominent at MgO(004) Bragg peak. It results from $d$-spacing difference between MgO substrate and NiO films. And, at low $q$ region, there is a phase shift and intensity reduction in the reflectivity of
solution environment (deionized water or 10 mM Pb contained solution), due to the existence of liquid phase
on the solid surface, relative to that of helium environment. As the modulus of liquid structure factor rapidly
decreases with $q^3$ the effect of existence of water phase on the observed intensity distribution is appearing only
within low $q$ range. Whether the ordering of liquid phases on the solid film is "layered" or follows "error-function"
is indistinguishable, however, due to the overwhelming film fringe signals. The difference in the reflectivity data
between de-ionized water and 10 mM Pb-contained solution in their intensity distribution is even smaller so that
they are hardly distinguishable. Although the experiment could be better tailored to possibly separate out the
critical difference between two liquid phases, we interpret the result as the MBE-grown nickel oxide is relatively
inert both in pure water and in Pb-contained solution at room temperature compared to that grown on Ni(110)
substrate.

Figure 3 shows the in-situ AFM images for as-grown NiO on Ni(110) and MBE grown NiO on MgO(001) in
air, water and 10 mM Pb-contained solution for 15 hrs. For the MBE grown NiO, the surface morphology shows
dense diamond shaped facets with root-mean-square (rms) roughness of 0.7 nm followed by round shapes in
water and Pb-contained solution with monotonous increase in rms roughness to 1.4 nm and 1.9 nm, respectively.
For as-grown NiO on Ni(110) substrate, in contrast, the morphology in air shows a flat surface with rms rough-
ness of $\approx 0.60$ nm. Large and small crater-shaped spots are randomly distributed on the surface. After exposure in
water for 15 hrs, the surface morphology changed to square shape due to the surface reconstruction by oxygen in
water. The rms roughness slightly increased to $\approx 0.88$ nm. In 10 mM Pb-contained solution, the surface was cov-
ered by crystallite particles with 0.1~0.3 μm size with drastic increase in rms roughness up to $\approx 17$ nm. As evident
from Fig. 3(c), the surface morphology underwent a significant change in Pb-contained solution. Figure 3(g)
shows the roughness changes in air, water and 10 mM Pb-contained solution for both samples. For the MBE
grown NiO, the roughness shows monotonous increase with change in environment from air to Pb-contained
solution, while, in the case of as-grown NiO, the roughness shows drastic increase between water and Pb con-
tained solution.

In order to investigate the role of X-ray irradiation in the drastic decrease of the X-ray reflectivity intensity
in water for as-grown NiO, we designed and performed continuous measurement of X-ray reflectivity of NiO
immersed in water near the Bragg peak ($L = 0.25$ r.l.u.) with and without X-ray irradiation for a given period of
time in an alternating manner as shown in Fig. 4(a). The red circles represent the measured intensity at each time,
and the orange and blue lines represent the exposure in water with and without X-ray irradiation, respectively.
Within 1 hr of immersion in water, the intensity decreases as a function of time even without X-ray irradiation
and saturates after 60 mins. After 7 hrs immersion without X-ray, no significant intensity drop was observed
before irradiation, while after exposure to X-ray, the intensity drastically started to drop and reached at a new sat-
uration value. Within additional 1 hr, the intensity drop was caused probably by the chemical interaction between
oxide and water until a certain saturation point. After saturation, the intensity was maintained whereas, after
irradiation for 10 mins, the intensity started to drop and reached a new saturation level.

At a glance on Fig. 4, it seems rather difficult to conclude whether X-ray takes a role for the chemical reaction
or not. Before further analyzing our data, it is worth mentioning relevant research reports on the role of X-ray
irradiation on the chemical reaction of the oxide layer with water. Synchrotron based X-ray beams can affect
the charge, bond and orbital states of strongly correlated systems. Furthermore, ionization of molecules by X-ray
can lead to radiolysis and formation of highly reactive free radicals. These radicals may then react chemically
with neighbouring materials even after the original radiation has stopped. However, most studies performed to explore
the effect of ionizing radiation and corrosion in nuclear materials was related to the $\gamma$-radiation, which has higher
energy than X-ray. For example, Daub et al. revealed that the rate of carbon steel corrosion depends on the
concentration of \( \text{H}_2\text{O}_2 \) which results from water radiolysis, and \( \text{OH}^- \) accelerates the corrosion process. Water radiolysis is the decomposition of water molecules due to the ionizing radiation, which creates \( ^*\text{HO} \) radical, \( \text{H}^* \) atom, \( \text{HO}_2^* \), \( \text{H}_3\text{O}^+ \), \( \text{OH}^- \), \( \text{H}_2\text{O}_2 \) and \( \text{H}_2 \). However, the X-ray energy that we used for our study is 17 keV, which is much lower than that used (~GeV) for the water radiolysis study. From this reasoning, we presumed that the beam damage of X-ray might be negligible.

To validate our presumption of negligible X-ray beam damage effect, we reorganized Fig. 4(a) so that we could compare the difference between the X-ray reflectivity intensities with and without X-ray exposure as shown in Fig. 4(b). Figure 4(b) shows the average reflectivity plot with and without X-ray exposure. We performed two-sample t-test to determine whether two samples are likely to have come from same two underlying populations that have the same mean. The p-value of our t-test is 0.635, much larger than the threshold value of 0.05, indicating that there is no significant statistical difference between the mean values of X-ray reflectivity with and without X-ray exposure. Furthermore, the X-ray reflectivity for the MBE grown NiO sample remained constant.

Figure 3. In-situ AFM images for as-grown NiO on Ni(110) (a–c) and MBE grown NiO on MgO(001) (d–f) in air (a), (d), water (b), (e) and 10 mM Pb-contained solution (c), (f) for 15 hrs, respectively. (g) Plot of roughness in each environment.
for more than a day. Therefore, we confirmed that X-ray did not affect the chemical reaction on the surface in our system.

As such, we can conclude that the different behaviors observed from two model systems, i.e., defect-free and defect-rich Ni oxide layers stem from the existence of the defects and neither from the bulk part of the oxide layer nor the external X-ray interacting with the water molecules. Indeed, the effect of defects on the chemical reaction between oxide film and water molecules has been reported by previous studies. Barbier et al. suggested that the chemical reaction of NiO(111) in water mainly takes place at defects, and Kitakatsu et al. claimed that the Ni(100) areas do not adsorb hydroxyl groups on regular sites but possibly on defect sites. Kofstad reported a comprehensive study on the importance of lattice, grain boundary and dislocation for metal oxide, but its defect structure and transport properties are still subject to considerable discussion.

Our results from X-ray reflectivity and AFM clearly show the difference in reaction with water between defective oxide and defect-free oxide. In case of the defect-free oxide, the oxide layer does not react with water and 10 mM Pb contained solution while defect-rich oxide underwent significant changes in morphology and interfacial structure. It clearly shows that the defect free oxide has stronger passivity than defect-rich oxide.

Other possible mechanisms responsible for our findings include the role of polycrystalline and/or amorphous phases. The existence of amorphous phase may facilitate the chemical reaction between oxide layer and either water or Pb-contained solution. However, further investigation is needed to clarify the effects of these phases on the chemical reaction of nickel oxide layer.

Conclusions

In summary, we investigated the role of defects in Ni oxide thin films on their chemical reaction in water and Pb contained solution. We used MBE grown NiO on MgO(001) substrate as the defect free NiO prototype, and NiO grown on Ni(110) single crystal as the one with defects. For the MBE grown NiO, we observed that the surface morphology changes in water and Pb-contained solution with monotonic increase in roughness. However, no significant changes were detected in the high-resolution X-ray reflectivity data. Meanwhile, in the case of native grown NiO on Ni(110), significant changes in both the morphology and atomistic structure at the interface were observed when immersed in water and Pb-contained solution. Furthermore, the reflected intensity decreased

![Figure 4.](a) Measured reflectivity intensity of NiO/Ni(110) with/without X-ray in water as function of time at L = 0.25 r.l.u. (near the Bragg peak). (b) Plot of average intensity drop with and without X-ray exposure.](a) Measured reflectivity intensity of NiO/Ni(110) with/without X-ray in water as function of time at L = 0.25 r.l.u. (near the Bragg peak). (b) Plot of average intensity drop with and without X-ray exposure.
with exposure time, implying that the chemical reaction of oxide layer initiates from the defect sites and continues until the oxide undergoes a full phase transition into nickel hydroxide phase.

Methods

Materials. Two types of samples were used in this study. One is native grown nickel oxide on Ni(110) single crystal, and the other is epitaxially grown (001)NiO on MgO(001) substrate by molecular beam epitaxy (MBE) method. The reason we used NiO(110) for polycrystalline sample was based on our findings that it contains grain boundaries and mixed amorphous and crystalline phases that are ideal for studying the effect of defects on the reaction of NiO surface with Pb-contained solution.29 And the reason we chose NiO(001) as our model system was because the epitaxially grown NiO(001) is the most studied system as well as the easiest to achieve epitaxial state close to single crystal.

Ni(110) single crystal (99.99%) with 10 mm diameter and 1.00 mm thickness was purchased from a commercial source (Princeton Scientific Corp.). The purchased sample surface was further mechanically polished with 0.03 μm alumina colloidal solution (pH ~3.5) followed by an electro-polishing with current density of 24.8 mA/mm² and −45 V for 50 s in mixture solution of 30% nitric acid – 70% methanol cooled by dry ice. After the electro-polishing, the sample was sputter-cleaned by Ar⁺ with 0.5 kV and 10 mA in 2.0 × 10⁻⁵ torr vacuum (10 mins) followed by annealing at 700 °C in 1.0 × 10⁻⁶ torr vacuum (5 mins) in an ultra-high vacuum (UHV) chamber at 33-ID-E beamline of Advanced Photon source (APS), Argonne National Laboratory. The sputtering and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to in-situ Reflection High-Energy Electron Diffraction and annealing procedure was repeated several times until an in-situ Reflection High-Energy Electron Diffraction (RHEED) pattern confirmed a homogenous single crystal surface. The cleaned surface was then exposed to

High resolution X-ray reflectivity. The native NiO layer grown on Ni(110) single crystal substrate was measured in helium environment and in bulk water using a thin-film cell, respectively, at room temperature. High resolution specular X-ray reflectivity measurements were performed at beamline 5-IDC of APS. The HRXR measurements basically scan the (00 L) crystal truncation rod (CTR) intensities along the surface normal direction, where L is the reciprocal lattice unit. The incident X-ray energy was 17.463 keV with ~8.0 × 10⁸ photons/sec beam flux. The reflected X-ray intensities were measured by Pilatus 100 K pixel array detector after 5 mm vertical and 5 mm horizontal slits. The background subtraction and the peak intensity integration were performed over ranges from L = 0.1 to 1.2 and d(22o) = 1.246 Å. As d/q relation, L = 1.2 corresponds to qmax = 6.0 Å⁻¹, which allows the real space features to be resolved with ~0.5 Å resolution.

For the MBE grown nickel oxide, we moved beamline from SID-C to 33BM-C due to the beam schedule. The range of L is from 0.1 to 2.2 and d(002) = 2.072 Å. Thus, L = 2.2 corresponds to qmax = 6.7 Å⁻¹. The incident beam energy was 17.864 keV with ~6.0 × 10⁸ photons/sec. High-resolution x-ray reflectivity was measured in helium, water, and 10 mM Pb-solution with varying pH conditions (3, 7 and 11).

In-situ atomic force microscopy (AFM). In order to investigate the surface morphology changes in air, water, and Pb-contained solution, the film surfaces were characterized by in-situ AFM using ac mode at Oak Ridge National Laboratory. The scan size was 1 μm × 1 μm and the scan rate was 0.8~1.2 Hz. All images were taken using ultrahigh frequency AFM probes with arrow shaped tip at the very end of cantilever coated by reflex aluminum.

References

1. Uberuaga, B. P., Vernon, L. J., Martinez, E. & Voter, A. F. The relationship between grain boundary structure, defect mobility, and grain boundary sink efficiency. Scientific Reports 5, 9095 (2015).
2. Chueh, W. C. & Haile, S. M. Electrochemical studies of capacitance in cerium oxide thin films and its relationship to anionic and electronic defect densities. Physical Chemistry Chemical Physics 11, 8144–8148 (2009).
3. Schneider, I. Z. et al. Synthesis, characterization, defect chemistry, and FET properties of microwave-derived nanoscaled zinc oxide. Chemistry of Materials 22, 2203–2212 (2010).
4. Kumar, A., Rajdev, D. & Douglass, D. L. Effect of Oxide Defect Structure on the Electrical Properties of ZrO2. Journal of the American Ceramic Society 55, 439–445 (1972).
5. Holloway, K. et al. Tantalum as a diffusion barrier between copper and silicon: failure mechanism and effect of nitrogen additions. Journal of Applied Physics 71, 5433–5444 (1992).
6. Steele, B. Oxygen ion conductors and their technological applications. Materials Science and Engineering: B 13, 79–87 (1992).
7. Macdonald, D. D. The history of the point defect model for the passive state: a brief review of film growth aspects. Electrochimica Acta 56, 1761–1772 (2011).
8. Kofstad, P. High temperature corrosion. Elsevier Applied Science Publishers, Crown House, Linton Road, Barking, Essex IG 11 8 JU, UK, 1988 (1988).
9. Bergholz, W., Mohr, W., Drewes, W. & Wendt, H. Defect-related gate oxide breakdown. Materials Science and Engineering: B 4, 359–366 (1989).
10. Palumbo, G. & Aust, K. Localization at grain boundary intersections in high purity nickel. Scripta metallurgica 22, 847–852 (1988).

11. Pan, Y., Adams, B., Olson, T. & Panayotou, N. Grain-boundary structure effects on intergranular stress corrosion cracking of alloy X-750. Acta Materialia 44, 4685–4695 (1996).

12. Tian, W., Du, N., Li, S., Chen, S. & Wu, Q. Metastable pitting corrosion of 304 stainless steel in 3.5% NaCl solution. Corrosion Science 85, 372–379 (2014).

13. Wijesinghe, T. S. L. & Blackwood, D. J. Real time pit initiation studies on stainless steels: the effect of sulphide inclusions. Corrosion Science 49, 1755–1764 (2007).

14. Pidaparti, R. M. & Patel, R. K. Investigation of a single pit/defect evolution during the corrosion process. Corrosion Science 52, 3150–3153 (2010).

15. Burstein, G., Liu, C., Souto, R. & Vines, S. Origins of pitting corrosion. Corrosion Engineering, Science and Technology 39, 25–30 (2004).

16. Parodi, A. et al. Corrosion behaviour of magnesium/aluminium alloys in 3.5 wt.% NaCl. Corrosion Science 50, 823–834 (2008).

17. Wang, Z.-W., Shu, D.-J., Wang, M. & Ming, N.-B. Diffusion of oxygen vacancies on a strained rutile TiO2 (110) surface. Physical Review B 82, 165309 (2010).

18. Marcus, P. Corrosion mechanisms in theory and practice. (CRC Press, 2011).

19. Masters, S. & Edwards, M. Increased lead in water associated with iron corrosion. Environmental Engineering Science 32, 361–369 (2015).

20. Graver, B. et al. Multilayer corrosion of aluminum activated by lead. Journal of The Electrochemical Society 157, C313–C320 (2010).

21. Lu, B. T., Luo, J. L. & Lu, Y. C. Correlation between film rupture ductility and PbSCC of Alloy 800. Electrochimica Acta 53, 4122–4136 (2008).

22. Peng, B., Lu, B. T., Luo, J. L., Lu, Y. C. & Ma, H. Y. Investigation of passive films on nickel Alloy 690 in lead-containing environments. Journal of Nuclear Materials 378, 333–340 (2008).

23. Lumsden, J. & McIlree, A. Factors affecting PbSCC in alloy 600 and alloy 690 steam generator tubing. (SFEN, 2006).

24. Herman, M. A & Sitter, H. Molecular beam epitaxy: fundamentals and current status. Vol. 7 (Springer Science & Business Media, 2012).

25. Chang, L. L. & Ploog, K. Molecular beam epitaxy and heterostructures. Vol. 87 (Springer Science & Business Media, 2012).

26. Arthur, J. R. Molecular beam epitaxy. Surface Science 500, 189–217 (2002).

27. Badyal, J. P. S., Zhang, X. & Lambert, R. M. A model oxide catalyst system for the activation of methane: Lithium-doped NiO on Ni(111). Surface Science 225, L15–L19 (1990).

28. Rieder, K. H. A combined SIMS-AES/LEED study of the room-temperature oxidation of Ni(110) and Ni(111) surfaces. Applications of Surface Science 2, 74–84 (1978).

29. Kim, J. et al. Multi-phase nickel oxide growth on Ni(110) surfaces. submitted (2017).

30. Dederichs, P. H. Theory Of Diffuse X-Ray-Scattering And Its Application To Study Of Point-Defects And Their Clusters. Journal of Physics F-Metal Physics 3, 471–496, doi: 10.1088/0305-4608/32/10 (2013).

31. Pantano, C. & Maday, T. E. Electron beam damage in Auger electron spectroscopy. Applications of Surface Science 7, 115–141 (1981).

32. Brown, N., Hewitt, J. A. & Meenan, B. J. X-ray-induced beam damage observed during x-ray photoelectron spectroscopy (XPS) studies of palladium electrode ink materials. Surface and Interface analysis 18, 187–199 (1992).

33. Fenter, P. & Sturchio, N. C. Mineral–water interface structures revealed by synchrotron X-ray scattering. Progress in Surface Science 77, 171–258 (2004).

34. Kuryukhin, V. et al. An X-ray-induced insulator-metal transition in a magnetoresistive manganese (1997).

35. Polli, D. et al. Coherent orbital waves in the photo-induced insulator–metal dynamics of a magnetoresistive manganese. Nature materials 6, 643–647 (2007).

36. Poccia, N. et al. Evolution and control of oxygen order in a cuprate superconductor. Nature materials 10, 733–736 (2011).

37. Analytis, J. G. et al. Atomic structure of the polar NiO (111)-p (2×2) surface. Physical review letters 96, 177002 (2006).

38. Daush, K., Zhang, X., Noé, J. & Wren, J. Effects of γ-radiation versus H 2 O 2 on carbon steel corrosion. Electrochimica Acta 55, 2767–2776 (2010).

39. Christensen, H. Effect of water radiolysis on corrosion in nuclear reactors. Radiation Physics and Chemistry 1755–1764 (2007).

40. Barbier, A. et al. Atomic structure of the polar NiO (111)-p (2×2) surface. Physical review letters 84, 2897 (2000).

41. Kitakatsu, N., Maurice, V. & Marcus, P. Local decomposition of NiO ultra-thin films formed on Ni (111). Surface Science 411, 215–230 (1998).

42. Kolstad, P. Defects and transport properties of metal oxides. Oxidation of metals 44, 3–27 (1995).

43. James, M. A. & Hibma, T. Thickness-dependent relaxation of NiO(001) overlayers on MgO(001) studied by X-ray diffraction. Surf. Sci. 433, 718–722, doi: 10.1016/S0039-6028(99)00476-8 (1999).

Acknowledgements

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science Laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under contract DE-AC02-06CH11357. Portions of this work (x-ray reflectivity data analysis) at Carnegie Institution of Washington, Pusan National University, and Ulsan National Institute of Science and Technology was supported by the International Collaborative Energy Technology R&D Program (No.20168540000030) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade Industry and Energy. The in-situ AFM experiments were conducted at Center for Nanophase Materials Sciences, which is a DOE Office of Science, Office of Basic Energy Sciences User Facilities. The XRR measurements were performed at sector 5ID-D (DND-CAT) and 33BM-C at Advanced Photon Source (APS). Work performed at the Center for Nanoscale Materials and the Advanced Photon Source at Argonne National Laboratory was supported by the DOE, Basic Energy Sciences, under Contract No. DE- AC02- 06CH11357. CP also acknowledges HPCAT supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775. J. D. H. and A. B. acknowledge support of the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division.
**Author Contributions**

J. Kim, C. Park, C.B. Bahn, J.H. Kim and S. Hong designed the experiments. J. Kim, C.B. Bahn, H. Hong, J. Hoffman, A. Bhattacharya prepared the samples. J. Kim, B. Hou, H. Hong, and C. Park performed HRXR experiments and analysis. J. Kim, J. Black, N. Balke, S. Hong performed AFM experiment and analysis. J. Kim, C. Park, H. Hong and S. Hong prepared the manuscript.

**Additional Information**

**Competing Interests:** The authors declare no competing financial interests.

**How to cite this article:** Kim, J. *et al.* Effect of defects on reaction of NiO surface with Pb-contained solution. *Sci. Rep.* 7, 44805; doi: 10.1038/srep44805 (2017).

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit [http://creativecommons.org/licenses/by/4.0/](http://creativecommons.org/licenses/by/4.0/)

© The Author(s) 2017