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Title: Evolution of thin protecting Si-layer on $Mn_{0.5}Si_{0.5}$ layer at low temperatures

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Highlights

Evolution of 2-nm-thick protecting Si-layer on $Mn_{0.5}Si_{0.5}$ film was studied by CAFM.

Many SiO_2 islands were found to form on the surface at 300℃.

Si cap layer first oxidized and then agglomerated into SiO_2 islands.

Protection capability of Si cap layer degraded after agglomeration of thin SiO_2 layer.

Mechanism of agglomeration of thin SiO_2 layer is discussed.

Evolution of thin protecting Si-layer on $Mn_{0.5}Si_{0.5}$ layer at low temperatures

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Evolution of 2-nm-thick protecting Si-layer on amorphous $Mn_{0.5}Si_{0.5}$ films at elevated temperatures was investigated by using conductive atom force microscopy (CAFM) and other structure and composition characterization methods. At a temperature of 300℃, a dramatic change was observed in surface morphology with many islands forming on the surface. Those islands were SiO_2 islands rather than Si ones. Further studies showed that those islands formed via first oxidation of the Si cap layer followed by the agglomeration of this SiO_2 layer. Because Si cap layer has widely been used as protecting materials to prevent the surface from oxidizing and contamination, this study provides an insight on the effectiveness of thin protecting Si-layer at low temperatures.

Keywords: surface protecting Si-layer, agglomeration, CAFM, ferromagnetic semiconductor

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1. Introduction

Surface protection is important for silicon industry, because incorporation of impurities from outside during subsequent processing will change material properties and degrade device performance in a variety of ways, including increasing the leakage current [1,2], changing energy band structures [3] and even having chemical reaction with bulk atoms [4,5]. It is well known that impurities (such as Fe [3], Au [6,7], Pt [6], Ag [7], etc. will produce deep levels in the band gap of Si and having large capture cross sections for carriers [8], which will greatly degrade the device performances.

For ferromagnetic semiconductor thin films, surface protection is especially important, since oxidation of surface of the films may totally alter their magnetic properties. Thus, a thin protecting cap layer will usually be grown on the top of the materials. For example, thin GaN layer was used to protect dilute magnetic semiconductors (DMSs) p-(Ga, Ni)N [9], a thin BeTe layer for DMSs p-$Be_{(1-x)}Mn_xTe$ [10], a thin ZnSe layer for $Zn_{0.97}Mn_{0.03}Te$ [11], etc.

Si is widely used as a common surface protecting material, since a native thin SiO_2 layer could well prevent further oxidation and is believed to be stable at low temperatures. Also, it is generally thought that a few nanometer-thick Si layer could serve as a good surface protecting layer. In our experiment, a 2-nm-thick Si layer was deposited on amorphous $Mn_{0.5}Si_{0.5}$ as a protecting layer. At the temperature of 300℃, a dramatic change in surface morphology was observed with many islands forming on the surface. As a result, the protection effectiveness of the Si cap layer degraded. Conductive atom force microscopy (CAFM) results indicate that these islands are

SiO_2 islands rather than Si ones. Further studies showed these islands formed via first oxidation of the Si cap layer followed by the agglomeration of this SiO_2 layer, rather than first agglomeration of the Si cap layer followed by oxidation. The possible reasons behind this agglomeration of the SiO_2 layer are discussed.

2. Experiments

P-type Si (001) substrates with a resistivity of ~20 Ω•cm were first cleaned by the Shiraki method and then loaded into an ultrahigh vacuum growth chamber (1.0×10^{-9} Torr). The substrates were then heated to 950℃ for 30 min to desorb surface oxide and a clean Si surface with 2×1 reconstruction pattern can be confirmed by reflection high-energy electron diffraction. After that, nearly 8-nm-thick $Mn_{0.5}Si_{0.5}$ film was deposited on Si substrates at room temperature in a molecular beam epitaxy (MBE) system, followed by 2-nm-thick or 8-nm-thick Si cap layer deposition. For comparison, one sample without Si cap layer was also grown at the identical conditions. Samples were annealed in vacuum at different temperatures (namely 200 and 300℃) for 1 h.

Surface morphologies and electrical conductivities of samples were investigated by a commercial scanning probe microscope (Multimode V, Bruke Nano Surface) in CAFM mode. In this mode, a voltage was applied between CAFM tip and sample, the current image is obtained simultaneously with atomic force microscopy (AFM) image. All the measurements are performed in a nitrogen atmosphere to avoid further

oxidiation during measurement. Microstructures and composition of samples were characterized by X-ray photoelectron spectroscopy (XPS) (instrument model, AXIS Ultra DLD) and high resolution transmission electron microscopy (HRTEM) (instrument model, FEI Tecani F30).

3. Results and discussion

Fig. 1 shows topography and current images of the samples with 2-nm-thick Si cap layer and annealed at different temperatures. For the as-grown sample, surface roughness is less than 1 nm. The current image is featureless with a current value of -10 nA at an applied voltage of -3 V (Fig. 1d), showing a good uniformity of the sample surface. For the sample annealed at 200℃, the surface morphology remains smooth (Fig. 1b), however, to obtain the same current, the applied voltage had to be increased to -4 V, which is due probably to a slightly increased thickness of surface SiO_2 layer after annealing (Fig. 1e).

For the sample annealed at 300℃, a striking change in surface morphology was observed, with apperance of many islands which are 200 nm in diameter and 10 nm in height, as shown in Fig. 1c. The surface of the sample became less conductive, -25 pA at a voltage of -6 V, and the islands became insulating with a much smaller current of -5 pA at the same applied voltage of -6 V, as marked with cycle in Fig. 1f. It implies that those islands may be SiO_2. In order to know what the islands are and how the islands formed, a comparative sample, a $Mn_{0.5}Si_{0.5}$ layer with the same thickness, but without Si cap layer, was grown and annealed under the identical conditions. The

surfaces of the as-grown sample and the samples annealed at different temperatures were almost the same, all being smooth. And the conduction of the surface greatly decreased after annealing at 300℃ but with featureless CAFM images (Fig. 2a-f). These results are in sharp contrast to those obtained on the surface with a Si cap layer, and clearly tell us that the formation of the islands is closely related to the Si cap layer.

In order to further investigate the mechanism of the formation of those islands and the constituents of those islands, surface chemical constituents of the samples which have different surface morphologies were studied by XPS measurements. Mn and Si XPS spectra were measured for the samples annealed at different temperatures. For the sample with 2-nm-thick Si cap layer, two sharp peaks, located at 649 and 638 eV, as shown in Fig. 3a, could be seen for all the annealed samples, which correspond to the $2p_{1/2}$ and $2p_{3/2}$ peaks of elemental Mn [12], respectively. Careful XPS spectrum examination could find that there are small humps (654 and 642 eV) for the sample annealed at 300 ℃, corresponding to the Mn oxidized state [13-16]. It means that the Si cap layer degraded its protection capability after annealing at 300 ℃, which correlates the agglomeration of the SiO_2 layer or the formation of many islands at this temperature as shown in Fig. 1c. Due to the agglomeration of the SiO_2 layer at this temperature, no SiO_2 layer was left in some regions on the surface of $Mn_{0.5}Si_{0.5}$ layer, the surface Mn in those regions would be oxidized. In contrast, for the sample without Si cap layer, as shown in Fig. 3b, the intensity of 2p peaks of oxidized Mn is much stronger than that of elemental Mn for both the as-grown and annealed samples. So, it

can be concluded that before the formation of SiO_2 islands, the 2-nm-thick Si cap layer could well protect the surface of the $Mn_{0.5}Si_{0.5}$ layer.

Fig. 3c shows the XPS spectra of Si 2p for the sample with a 2-nm-thick Si cap layer. Two sharp peaks, located at 99 and 103 eV, could be seen in all the annealed samples, which correspond to elemental and oxidized Si, respectively. According to the peak position of 103 eV, the oxidized Si is attributed to be SiO_2. For the sample annealed at 300℃, the peak at 99 eV for the as-grown sample shifted to 98 eV, suggesting the formation of manganese silicide MnSi, since the binding energy of Si 2p in the manganese silicide MnSi is slightly smaller than that of Si 2p in elemental Si [17-19]. The formation of manganese silicide MnSi was confirmed by TEM observation results, which will be shown later. For comparison, Fig. 3d shows XPS spectra of Si 2p of the samples without Si cap layer, no shift in elemental Si 2p peak position was observed for the sample annealed at 300℃.

Based on the above XPS results, only five kinds of molecules or atoms could exist on the surface of the sample with a 2-nm-thick Si cap layer and after annealing at 300℃, namely manganese, silicon, manganese oxides, silicon dioxide and manganese silicide. In view of the nonconducting properties of islands in CAFM current images, the islands are believed to be SiO_2 islands. To prove the conclusion, we used 5% hydrofluoric acid, which only etchs SiO_2, to dip this sample for 20 seconds. After the dip, almost no islands remained, as shown in Fig. 4a, confirming that the islands are SiO_2 rather than Si islands. The removal of surface SiO_2 lead to a better electrical conduction of the sample, the applied voltage for the same current value was much

reduced as shown in Fig. 4b.

The next question we have to answer is how the SiO_2 islands formed. Firstly, the Si atoms in the SiO_2 islands come from the Si cap layer not from the $Mn_{0.5}Si_{0.5}$ layer, which was evidenced by the comparative results obtained from the sample without Si cap layer. As shown in Fig. 2c, no island formed for this sample after annealing at 300℃, which clearly confirmed the above conclusion. Secondly, there are two possible ways for the formation of the SiO_2 islands. One way is as follows, at 300℃ the Si cap layer first oxidized to SiO_2, then the SiO_2 layer agglomerated to the SiO_2 islands. The other way has a different process. The Si cap layer first agglomerated to Si islands, then the Si islands oxidized to SiO_2 islands. To distinguish two ways, another sample with a 2-nm-thick Si cap layer was prepared. This sample was in-situ annealed in the growth chamber at 300℃, in which not much oxygen is available for the oxidation of surface Si. As shown in Fig. 5a, this sample has a very smooth surface, no islands forming on the surface, which excludes the possibility of the second way mentioned above for the formation of SiO_2 islands. Moreover, after this sample was reannealed in a vacuum furnance(3×10^{-6} Torr) at 300℃, islands appeared on the surface as shown in Fig. 5b, which implies that the formation of the SiO_2 islands took place after or during the oxidation of the Si cap layer at 300℃.

However, the mechanism for the agglomeration of the SiO_2 layer was not understood yet. Fig. 6a shows the cross-sectioned HRTEM image of the sample with the SiO_2 islands. No SiO_2 islands could be observed on the top of $Mn_{0.5}Si_{0.5}$ layer, which may be due to a low contrast or desorption of SiO_2 during the cross-sectional

TEM sample preparation. A clear lattice image of the $Mn_{0.5}Si_{0.5}$ layer was observed. Compared with the lattice spacing of substrate Si in Fig. 6b, the lattice parameter of $Mn_{0.5}Si_{0.5}$ layer was measured to be 0.454 nm, being consistent with the cubic MnSi lattice constant (a=0.456 nm) [20-24]. As mentioned before, both the $Mn_{0.5}Si_{0.5}$ layer and the Si cap layer were deposited on the substrate at room temperature. Both layers have amorphous structures due to the low deposition temperature, which were confirmed by Raman spectra (not shown here). At the annealing temperature of 300℃, solid phase epitaxy growth from the Si substrate would take place, the $Mn_{0.5}Si_{0.5}$ layer became a single crystal layer. A schematic for the evolution of 2-nm-thick Si cap layer at different annealing temperatures is shown in Fig. 7. After the solid phase epitaxy growth of MnSi, the interface energy between SiO_2 layer and crystalline MnSi layer may become high. It is the high SiO_2/c-MnSi interface energy that faciliates the agglomeration of the SiO_2 layer. The agglomeration of a thin SiO_2 layer truly depends on the interface structure or energy. When the Si cap layer thickness is 8 nm, which is much thicker than 2 nm, after the solid phase epitaxy growth from Si substrate at 300℃, the previous interface structure of a-Si/a-MnSi/c-Si would become a-SiO_2/c-Si/c-MnSi/c-Si. In this case, no SiO_2 islands were observed, as shown in Fig. 8a. Consequently, no oxidized Mn signal was observed in the XPS spectra as shown in Fig. 8b. So, the interface structure of the SiO_2 layer play a key role for the SiO_2 islands formation via agglomeration of a thin SiO_2 layer.

4. Conclusion

In conclusion, the evolution of a 2-nm-thick protecting Si-layer on $Mn_{0.5}Si_{0.5}$ film at elevated temperatures was investigated by using CAFM and other characterization methods. At a temperature of 300℃, a dramatic change in surface morphology was observed, many islands forming on the surface. Consequently, the protection effectiveness of the Si cap layer degraded. Those islands were found to be SiO_2 islands rather than Si islands, and are believed to form by the agglomeration of a thin surface SiO_2 layer, rather than by oxidation of Si islands. The driving force for agglomeration of the thin SiO_2 layer is speculatively attributed to a high SiO_2/c-MnSi interface energy. Since Si is widely used as a common surface protection material to prevent the surface from oxidizing and contaminating, this study provides an insight on the effectiveness of thin protecting Si-layer at low temperatures.

Acknowledgements

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Figure Captions

Fig. 1. Topographic and current images of the samples with a 2-nm-thick Si cap layer and annealed at different temperatures taken by CAFM. (a) Topographic and (d) current images of the as-grown sample taken at a sample bias of -3 V. (b) Topographic and (e) current images of the sample annealed at 200 ℃ taken at a sample bias of -4 V. (c) Topographic and (f) current images of the sample annealed at 300 ℃ taken at a sample bias of -6 V. All the images are taken at the same size.

Fig. 2. Topographic and current images of the sample without Si cap layer and annealed at different temperatures. (a) Topographic and (d) current images of the as-grown sample taken at a sample bias of -2 V. (b) Topographic and (e) current images of the sample annealed at 200℃ taken at a sample bias of -2 V. (c) Topographic and (f) current images of the sample annealed at 300℃ taken at a sample bias of -2.5 V. All the images are taken at the same size.

Fig. 3. XPS spectra of (a) Mn 2p and (c) Si 2p for the sample with a 2-nm-thick Si cap layer and annealed at different temperatures. XPS spectra of (b) Mn 2p and (d) Si 2p for the sample without Si cap layer and annealed at different temperatures.

Fig. 4. (a) Topographic and (b) current images of the sample with a 2-nm-thick Si cap layer, annealed at 300℃, and after being dipped by 5% hydrofluoric acid for 20

seconds. Topographic and current images were taken by CAFM at a sample bias of -0.5 V.

Fig. 5. Topographic images of the sample (a) before and (b) after a reannealing in a vacuum furnace (3×10^{-6} Torr) at 300℃. The sample was with a 2-nm-thick Si cap layer and previously in-situ annealed at 300℃ in the growth chamber.

Fig. 6. (a) HRTEM image of the sample with a 2-nm-thick Si-layer and annnealed at 300℃. (b) Enlarged HRTEM image of the region enclosed by a rectangle in (a).

Fig. 7. Schematic for the evolution of a 2-nm-thick Si cap layer at different annealing temperatures.

Fig. 8. (a) AFM image of the sample with a 8-nm-thick Si cap layer and annealed at 300 ℃. (b) XPS spectra of Mn 2p for this sample.

Figure1

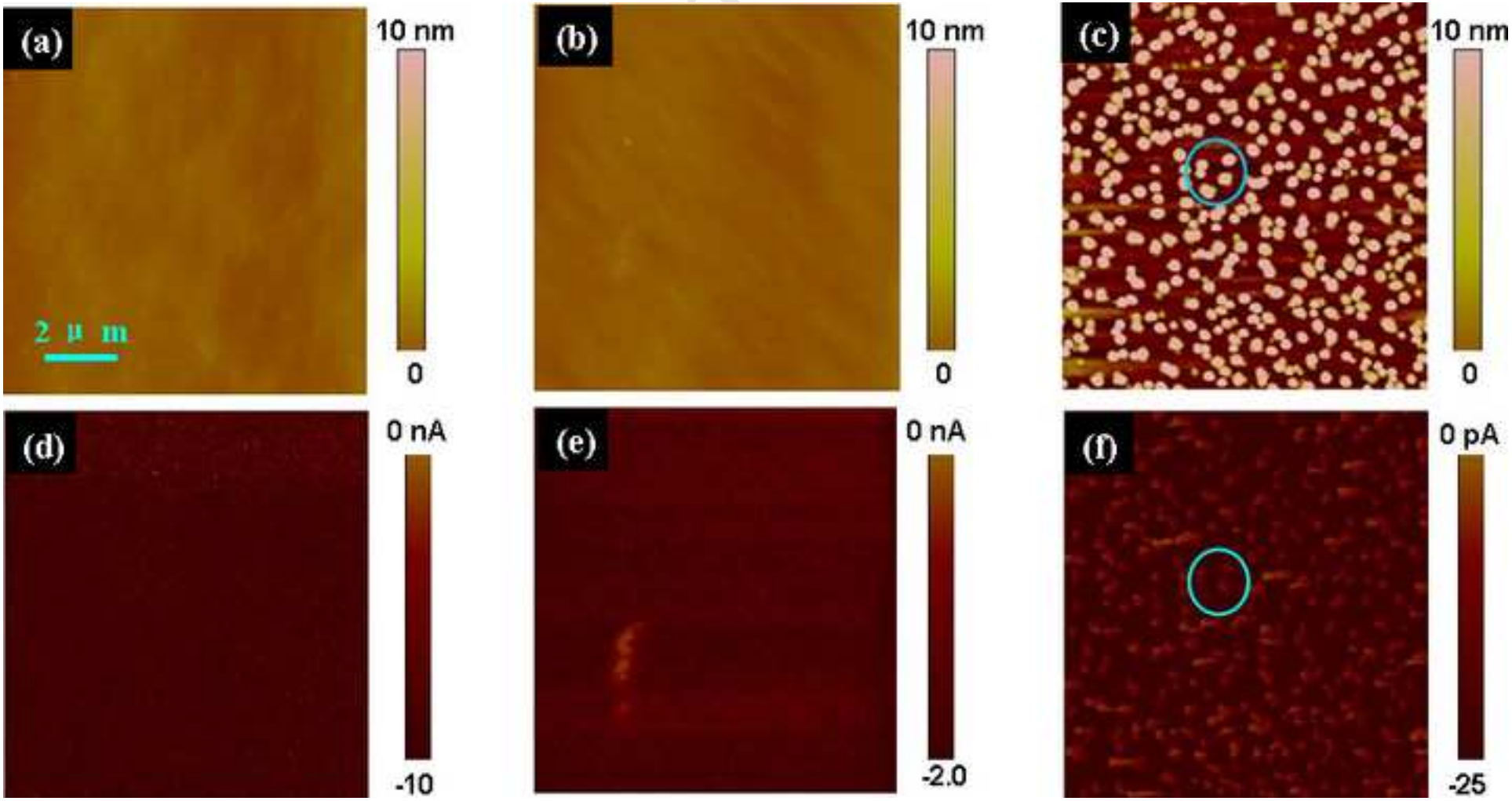


Figure2

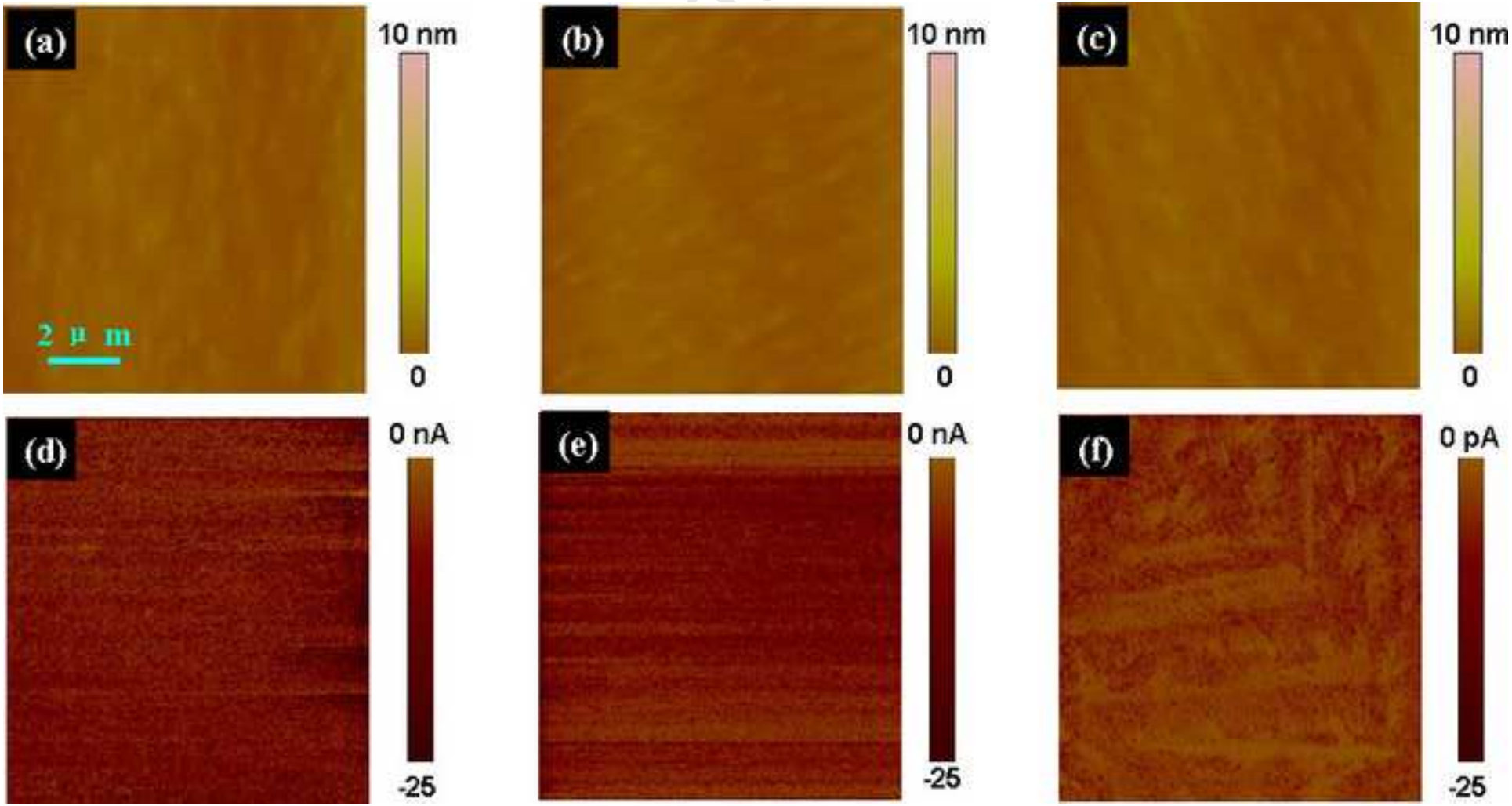
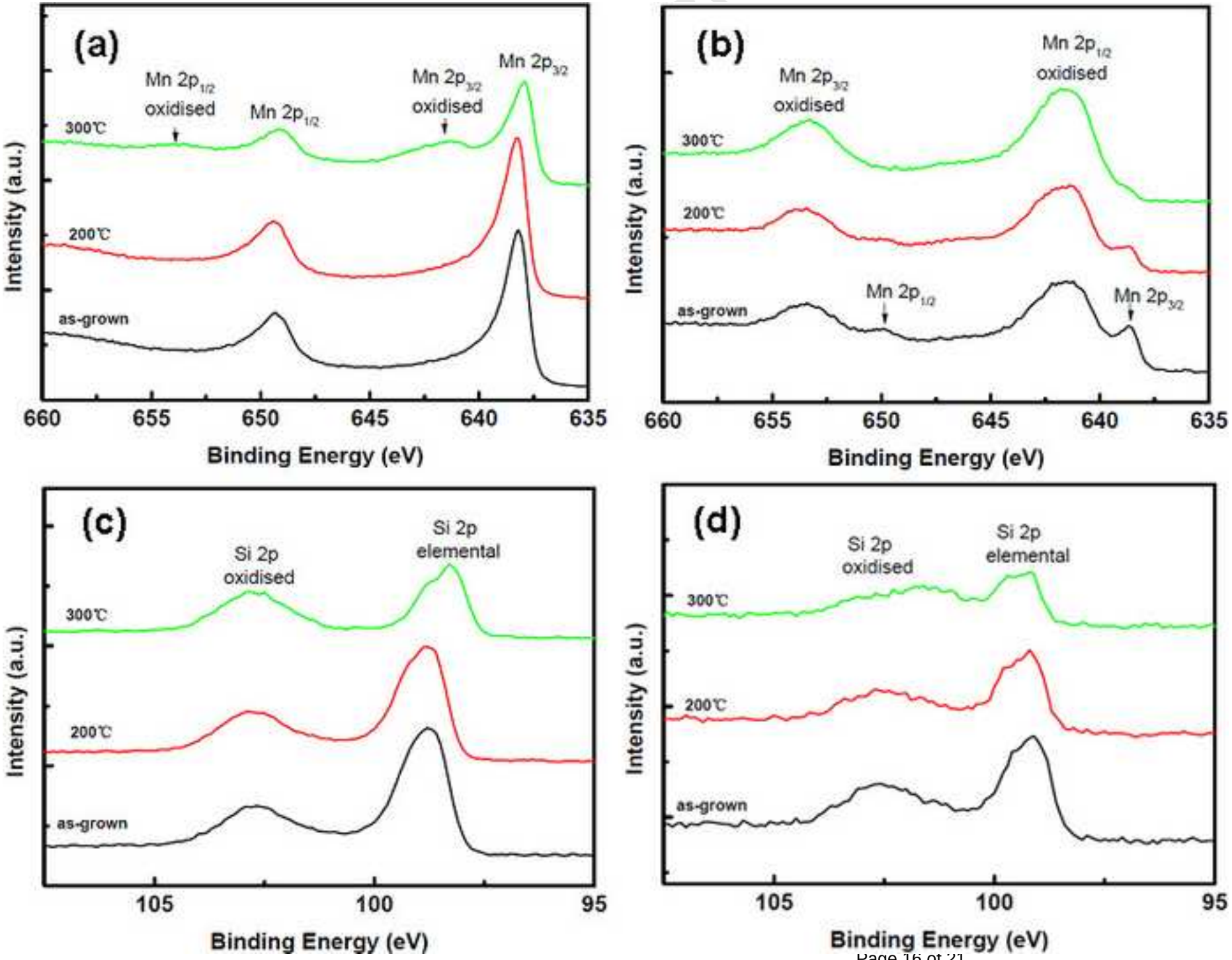


Figure3


(a)
Mn 2p1/2 oxidised
Mn 2p1/2
Mn 2p3/2 oxidised
Mn 2p3/2
300℃
200℃
as-grown
Intensity (a.u.)
660
655
650
645
640
635
Binding Energy (eV)
(b)
Mn 2p3/2 oxidised
Mn 2p1/2 oxidised
300℃
200℃
as-grown
Mn 2p1/2
Mn 2p3/2
Intensity (a.u.)
660
655
650
645
640
635
Binding Energy (eV)
(c)
Si 2p oxidised
Si 2p elemental
300℃
200℃
as-grown
Intensity (a.u.)
105
100
95
Binding Energy (eV)
(d)
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Si 2p elemental
300℃
200℃
as-grown
Intensity (a.u.)
105
100
95
Binding Energy (eV)

Figure4

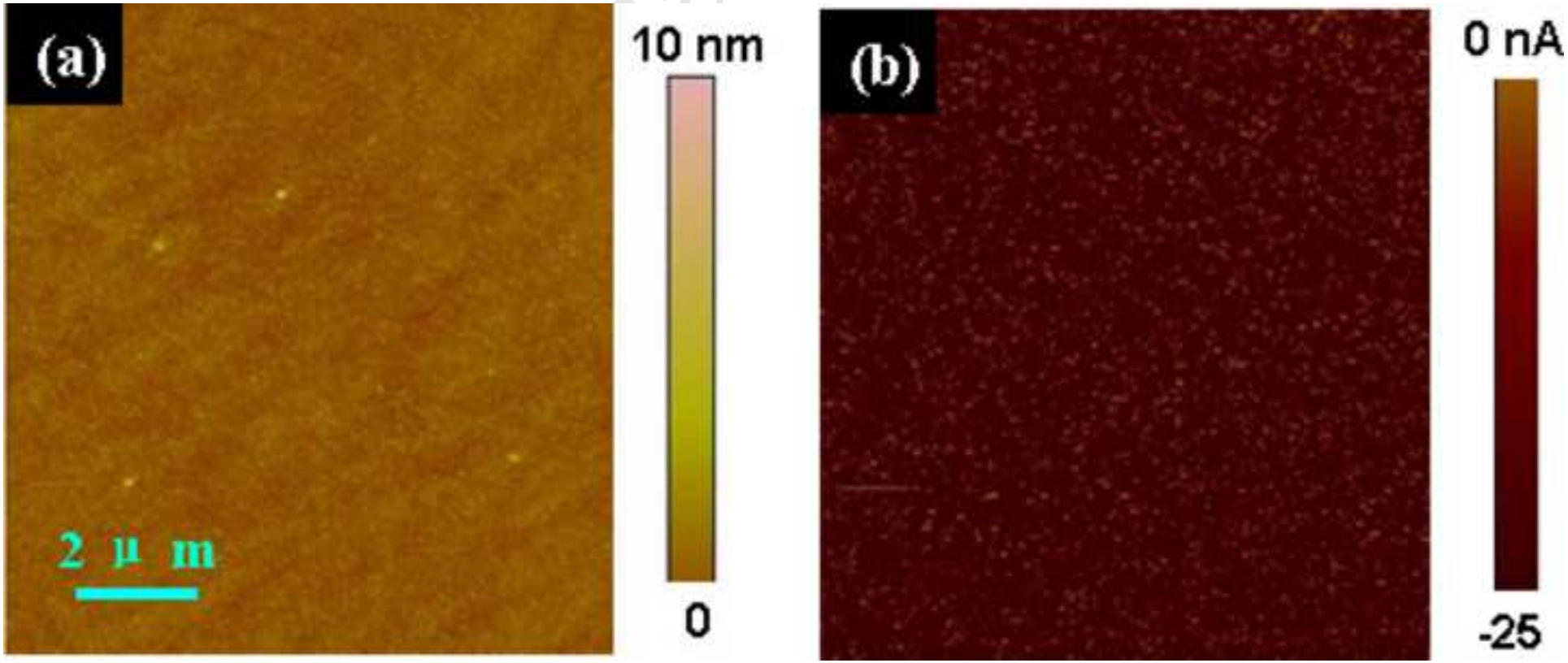


Figure5

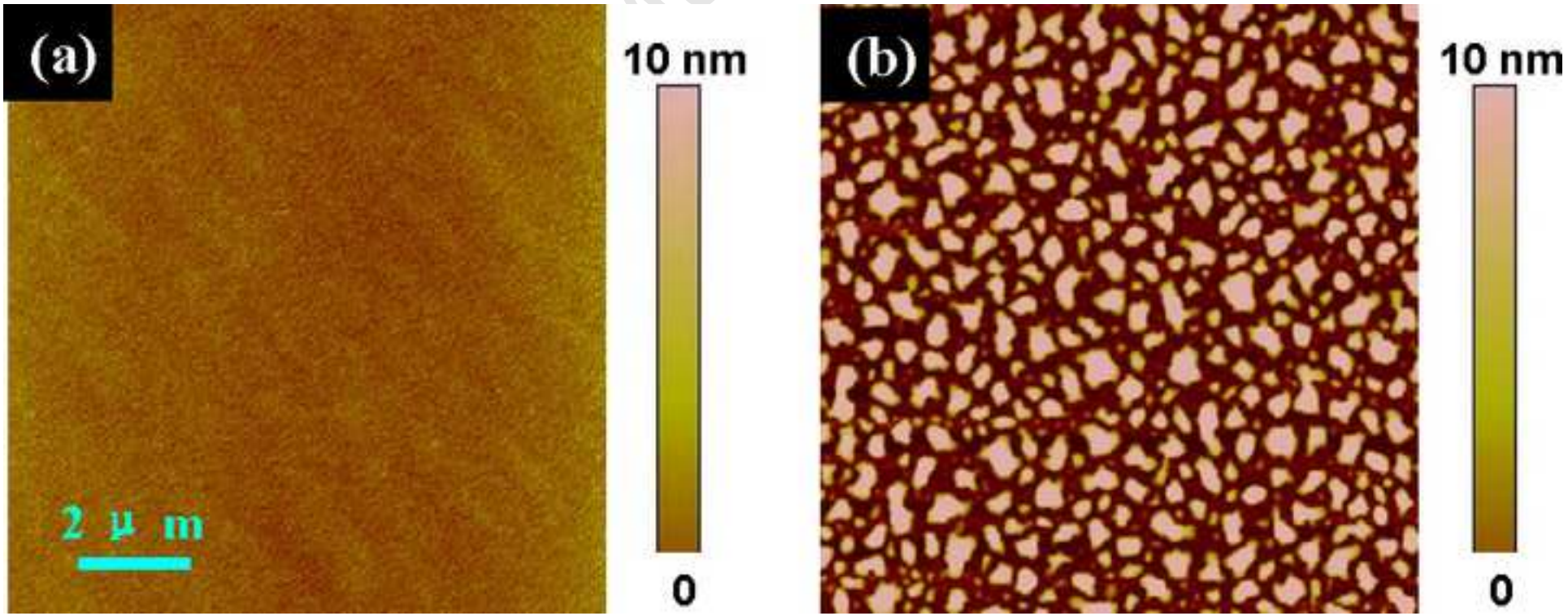


Figure6

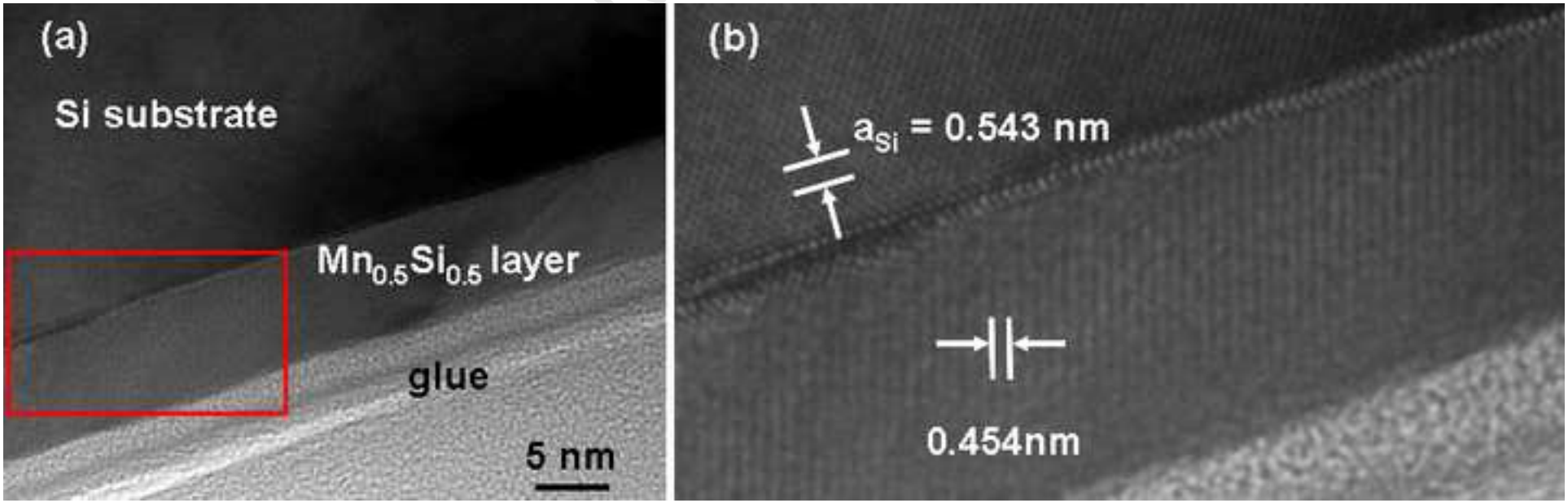


Figure7

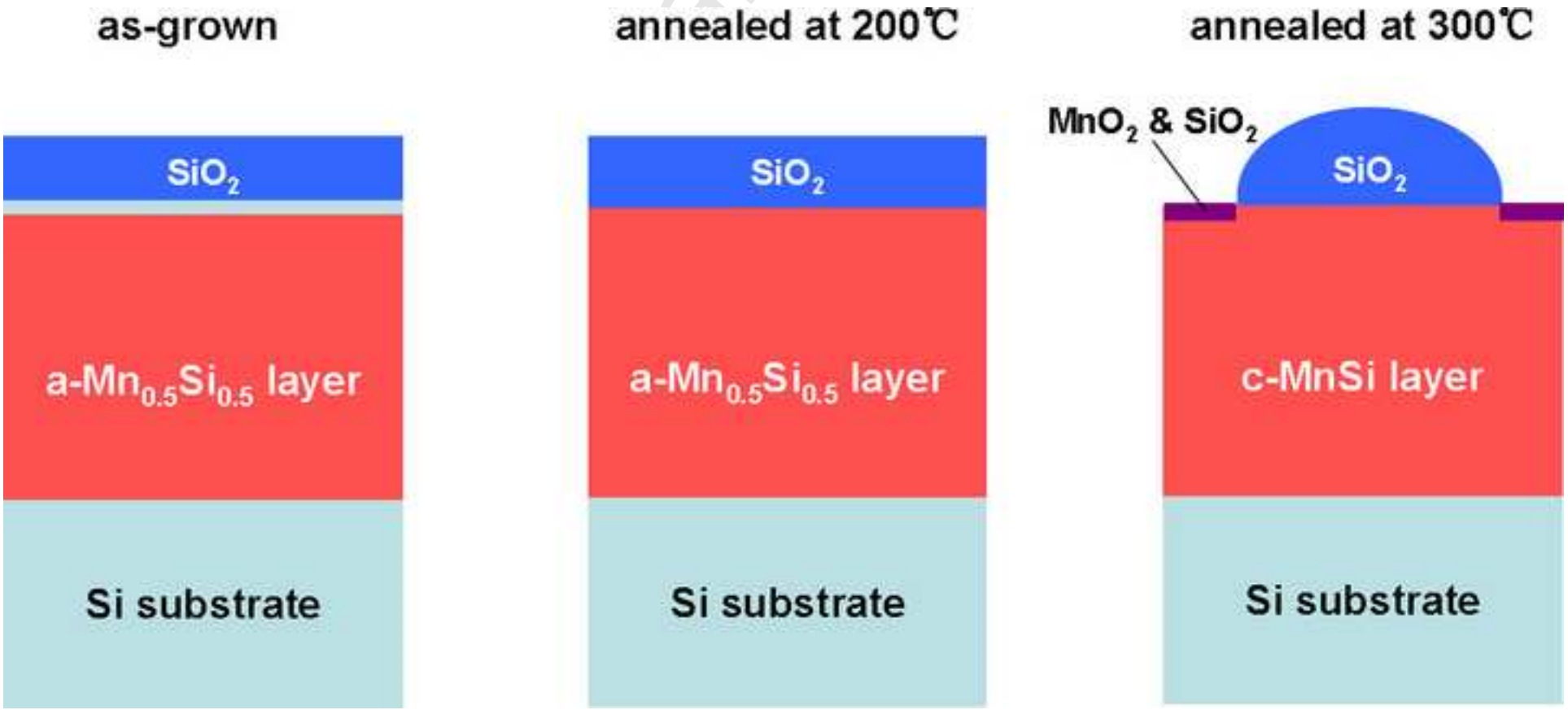
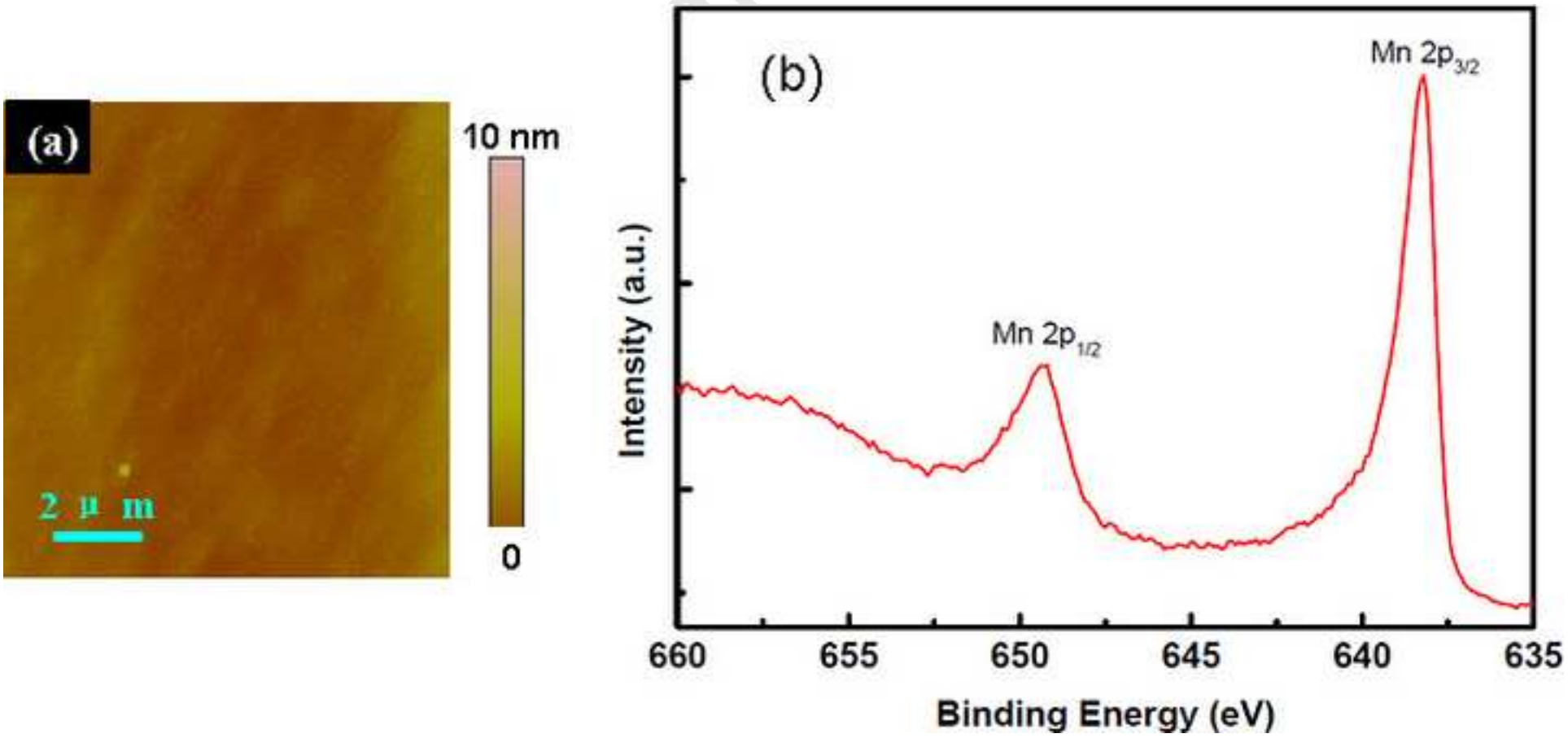

as-grown
annealed at 200℃
annealed at 300℃
SiO2
a-Mn0.5Si0.5 layer
Si substrate
SiO2
a-Mn0.5Si0.5 layer
Si substrate
MnO2 & SiO2
SiO2
c-MnSi layer
Si substrate

Figure8


(a)
10 nm
0
2 μ m
(b)
Mn 2p3/2
Mn 2p1/2
Intensity (a.u.)
660
655
650
645
640
635
Binding Energy (eV)