***In situ* studies on radiation tolerance of nanotwinned Cu**

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Abstract

We investigate the radiation response of nanotwinned Cu by using *in situ* Kr ion irradiation technique inside a transmission electron microscope. In comparison with coarse grained Cu, nanotwinned Cu exhibits smaller defect size and lower defect density. *In situ* studies also show that twin boundaries effectively remove a large number of defect clusters. The lifetime of defect clusters in nanotwinned Cu is very different from that in its coarse grained counterpart. This study provides further evidence on twin-boundary enabled radiation tolerance in nanotwinned metals.

Keywords: nanotwins, radiation damage, *in situ*, defect kinetics

1. Introduction

Irradiation of metallic materials by neutrons or heavy ions results in a large number of vacancy and interstitial clusters. Typical defect clusters include stacking fault tetrahedra (SFTs), Frank loops, dislocation loops and voids [1-7], which tend to grow further under continuous radiation process, causing severe degradation of mechanical properties in irradiated metallic materials [8-10]. To alleviate radiation damage in these materials, various types of defect sinks have been studied, including grain boundaries, phase boundaries and twin boundaries. Grain boundary is one of the primary defect sinks that can effectively reduce radiation induced defect density [11-16] and curtail void swelling [17-24]. Phase boundaries in ferritic/ martensitic steels [25-27], oxide dispersion strengthened (ODS) alloys [28, 29] and nanolayered structures [30-34] have also attracted increasing attention as these boundaries can be effective defect sinks.

Nanotwinned (nt) metals have also shown enhanced radiation tolerance due to the existence of high-density twin boundaries (TBs) [35-38]. Niewczas and Hoagland [39] predicted the deconstruction of SFTs by mobile TBs in Cu by atomistic simulations. Recently, we have reported *in situ* observations of the removal of SFTs by nanotwins in Kr ion irradiated nt Ag [40, 41]. A twin boundary affected zone was also discovered wherein time accumulative defect density and defect diffusivity were substantially different from those in twin interior [42]. Furthermore we show that deliberate introduction of nanovoids in conjunction with nanotwins enables significantly enhanced damage tolerance in nt Cu. TBs can provide fast diffusion channels for radiation induced defects, and nanovoids store and annihilate a large number of defect clusters. As a result, instead of experiencing void growth (or void swelling) that are frequently observed

in irradiated conventional metals, these pre-existing voids at twin boundaries shrink by absorbing radiation induced interstitial loops as revealed by *in situ* Kr ion irradiation studies [43].

Radiation damage in Cu, as a model system, has been intensely investigated by both *ex situ* [44], [45] and *in situ* radiation experiments [46, 47]. As Cu has a low stacking fault energy, a majority of the radiation induced defects are SF Ts [3, 8]. Subsequently, systematic studies were reported on the formation of SFTs [48-50] and destruction/annihilation of SFTs by mobile dislocations [51-55]. The role of TBs in Cu has been scatterly discussed in literature [38, 45, 47]. In order to further elucidate the interaction of defect clusters with TBs, we performed *in situ* Kr ion irradiation studies on cross-sectional specimens of nt Cu inside a transmission electron microscope. Our *in situ* studies provide ample evidence for defect-TB interactions, including the absorption of defect clusters by TBs. Furthermore our statistical studies show that the defect life time is drastically changed when they are adjacent to TBs, lending further support for the significance of TBs on removal of defect clusters in metals.

2. Experimental

Cu films were deposited on HF etched Si (110) substrates using the magnetron sputtering technique at room temperature. The chamber was evacuated to a base pressure of less than 8×10^{-8} torr prior to deposition. The total film thickness was $\sim 1 \mu\text{m}$ for nt Cu and $\sim 20 \mu\text{m}$ for coarse grained (cg) Cu. The deposition rate was $\sim 0.5 \text{ nm/s}$. Cg Cu film was peeled off from substrates after deposition and annealed in vacuum of less than 6×10^{-7} torr at 300°C for 1 h, followed by subsequent furnace cooling. Cross-sectional transmission electron microscopy (XTEM) samples

were prepared by dimpling and low energy (3.5 keV) Ar ion milling and subsequent ion polishing.

In situ Kr⁺⁺ ion irradiation at 1 MeV was performed for cg and nt Cu at room temperature in the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory, where an ion accelerator was attached to a HITACHI H-9000NAR transmission electron microscope. The microscope was operated at 200 kV continuously during radiation in order to record the microstructural evolution. The average dose rate was $0.43\text{--}1.98 \times 10^{-3}$ dpa s⁻¹. A CCD camera was used to capture microstructural evolution during radiation at 15 frames s⁻¹. The Stopping and Range of Ions in Matter (SRIM) simulation was used to estimate the displacement damage profile and Kr⁺⁺ ion distribution [56]. High resolution TEM (HRTEM) experiments were performed using an FEI Tecnai G2 F20 microscope operated at 200 kV. The density and size of radiation induced defects at each individual radiation dose shown in Fig. 4 were measured by using three TEM micrographs with the size of $\sim 200 \times 200$ nm². The error bars were determined by standard deviations. In Fig. 7 and Fig. 8, for the stage 1, the statistical data of defect life time for both cg and nt Cu were collected from the dose range of 0 – 0.025 dpa ; in the stage 2, the statistical data of defect life time for both cg and nt Cu were collected over the dose of 1.4–1.5 dpa. Error bars for defect lifetime were determined from standard deviation.

3. Results

Fig. 1 shows the microstructural evolution of cg Cu subjected to Kr ion irradiation. The as-annealed cg Cu (Fig.1 a) contained little growth defects, which were formed during sputtering deposition. The defect density drastically increased after radiation to a low dose of ~ 0.01 dpa, as

shown in Fig. 1b. The average defect size was ~ 6.5 nm. Radiation led to continuous growth of defect clusters, some of which had dimensions of 20 nm by 0.05 dpa as shown in Fig. 1c. By 1.56 dpa, large defect clusters as well as dislocation segments were frequently observed as labeled in Fig. 1d.

In comparison, nt Cu exhibited significantly different morphology. High-density growth twins with $\Sigma 3$ {111} coherent twin boundaries (CTBs) and $\Sigma 3$ {112} incoherent twin boundaries (ITBs) were observed in as-deposited nt Cu (Fig. 2a), showing an average twin thickness of ~ 15 nm. Although there were a few growth defects in the as-deposited specimen, the increment rate of defect density was significantly lower than that in cg Cu. Up to 0.1 dpa, the defect density remained low as shown in Fig. 2b. By 0.56 dpa, radiation triggered extensive interaction between TBs and defect clusters and led to the formation of stacking faults (SFs) at TBs as shown in Fig. 2c. By 1.56 dpa little dislocation segments were observed (Fig. 2d).

Fig. 3 compares defect morphology among cg Cu (Fig. 3a), thick twinned Cu (Fig. 3b) and fine twinned Cu (Fig. 3c). After radiation, cg Cu (Fig. 3a) contained very large defect clusters (~ 20 nm in size). In thick twinned Cu, abundant defect clusters were observed, which were mainly in the form of intact SFTs (Fig. 3b2). In the irradiated fine nt Cu, truncated SFTs as outlined in Fig. 3c2 were frequently observed near TBs. Furthermore SFs were identified adjacent to the TBs. Correspondingly the streaking lines in the inset fast Fourier transform (FFT) of the image also confirm the formation of SFs.

Comparison of the defect density in the cg and nt Cu is shown in Fig. 4a. In both cases, defect density increased rapidly in the early radiation stage (stage 1) and then reached a plateau (in stage 2). Several significant differences were also noted. (1) In the stage 1, the increment rate

of defect density in cg Cu is much higher than that in nt Cu. (2) The saturation defect density in nt Cu is ~50% of that in cg Cu. Comparison of the distributions of defect dimension in Fig. 4b (up to 1.56 dpa) shows that cg Cu has a broad range of defect size, varying from 2-17 nm, with an average dimension of ~ 6 nm. In contrast nt Cu has an average defect size of ~ 3 nm, with a smaller size distribution, in the range of 1-9 nm.

In situ snapshots in Fig. 5 (see Supplementary Video S1) illustrate the formation of large defect clusters in cg Cu. The initial dislocation segment 1 (Fig. 5a) interacted with the newly formed segment 2 (Fig. 5b) by 7s. The two intersecting dislocation segments absorbed peripheral defects continuously to form a larger dislocation tangles (Fig. 5c) by 31s. The dislocation tangle eventually evolved into a large circular defect cluster (Fig. 5d).

In contrast the evolution of defect clusters in nt Cu is clearly curtailed by TBs. *In situ* videos captured direct and representative evidence for the absorption of dislocation loops by TBs during radiation of the nt Cu over 0.3-0.4 dpa (see Supplementary Video S2). As shown in Fig. 6a, a radiation induced dislocation loop with ~ 4 nm in diameter was located in the middle of a laminate between two TBs. In 0.1 s, the loop migrated by nearly 4 nm towards the TB (Fig. 6b). Interestingly the loop was not immediately absorbed by the TB and it did not grow either during continuous radiation. After 8s, the loop was merely 3 nm away from the TB (Fig. 6c) and nearly contacted the TB by 8.2 s (Fig. 6d). The loop was then in full contact with the TB and became smaller by 9.1 s (Fig. 6e). Finally by 11.2 s, the entire loop was annihilated by the TB.

The kinetics of defect evolution in nt Cu was studied by examination of hundreds of defect clusters from the *in situ* radiation videos. Within a certain range of radiation dose, the migration behaviors of a large number (hundreds) of newly generated defects were tracked

individually and manually to obtain the location and life time of these defects. In particular, the life time of defect clusters as a function of their distances to TBs is plotted in Fig. 7. In the stage 1, the average defect life time is ~ 19 s with insignificant dependence on the distance to TB, although the defect life time appears to decrease slightly to 10 s when they are very close (within 5 nm) to the TBs. In the stage 2, the average defect life time decreases sharply to 4 s, with little dependence on their distance to TBs (when the separation distance is 20 nm or less).

Meanwhile, the life time of defect clusters in the stage 2 as a function of defect size is compared between the cg and nt Cu. As shown in Fig. 8, the nt Cu with smaller defect cluster size (1-5 nm) has a very short average defect life time, ~ 4 s. However, the average life time of defect clusters (5-11 nm) in cg Cu is ~ 15 s. The average life time and defect sizes for the cg and nt Cu are summarized in Table 1. The corresponding accumulated dose of life time of defect clusters is also provided.

4. Discussion

4.1 Formation of SFTs and loops

Interstitial clusters can transform into faulted Frank loops and perfect loops[57], while vacancy clusters are in the form of SFTs and Frank loops on {111} planes [49]. The energy of a mixed dislocation loop can be calculated by [7, 58]

$$E_{loop} = \frac{\mu b_e^2 r_L}{2(1-\nu)} \ln \left[\frac{2r_L}{r_0} \right] + \frac{\mu b_s^2 r_L}{2(1-\nu)} \left(1 - \frac{\nu}{2} \right) \ln \left[\frac{2r_L}{r_0} \right] \quad (1),$$

where the first term on the right corresponds to the elastic energy of a circular edge loop with radius r_L in an isotropic solid with Burgers vector b_e , and the second term is the elastic energy of a screw loop with Burgers vector b_s . The cut-off distance here is $2r_L$ because the stress fields of dislocation segments on opposite sides of a loop cancel at a distance of $\sim 2r_L$. For the perfect loop, $b = 1/2 \langle 110 \rangle$, so that $b_e^2 = a^2/3$ and $b_s^2 = a^2/6$. For the Frank loop, $b_e^2 = a^2/3$ and $b_s^2 = 0$. In addition, the Frank loop contains a stacking fault with energy of $\pi r^2 \gamma_{SF}$, where γ_{SF} is stacking fault energy, ~ 55 mJ/m² for Cu [59]. For Cu, $\mu = 48$ GPa, $b = 0.256$ nm, $\nu = 0.34$. The relationship between r_L with certain number of vacancies/interstitials (n) is

$$r_L = \left(\frac{\sqrt{3}a^2 n}{4\pi} \right)^{1/2} \quad (2),$$

where a is the lattice parameter (3.615 Å for Cu).

Now we can compare the calculated energy of a perfect and Frank dislocation loop as a function of the loop size (represented by the number of vacancies/interstitials) in the defect cluster. As shown in Fig. 9, when the radius of a loop (r_{loop}) is less than 16 nm, the energy of a Frank loop (E_f , represented by the blue dash-dotted line) is comparable to or slightly lower than that of a perfect loop (E_p , shown as the solid red line), indicating that Frank loops may be more stable than perfect loops in Cu. In this study, most of defect clusters have radius smaller than 16 nm, therefore the formation of Frank loops is energetically favorable.

Next we probe the formation of SFTs. The energy of an SFT can be estimated by [7]

$$E_{SFT} = \frac{\mu L b^2}{6\pi(1-\nu)} \ln \left[\left(\frac{4L}{a} \right) + 1.017 + 0.97\nu \right] + \sqrt{3} L^2 \gamma_{SF} \quad (3),$$

where L is the ledge length of an SFT and can be written as

$$L = a(n / 3)^{1/2} \quad (4).$$

Here a and n carry the same meaning as defined previously. As shown by the black solid line in Fig. 9, the energy of SFTs is much lower than E_F and E_P , implying that the formation of SFTs is energetically favorable over Frank and perfect dislocation loops, consistent with our *in situ* TEM observations.

4.2. Kinetics of defect clusters – defect life time

The difference between the life times of defect clusters in nt Cu in the two stages (as shown in Fig. 7) indicates that TBs play a significant role in the defect removal process. During the initial radiation process (stage 1), defect density is low and defect clusters seldom interact with TBs or among themselves. Consequently the life time of defect clusters is relatively long, ~ 19 s. In stage 2, the high defect density in twin interior prompts these defect clusters to interact actively and frequently with the TBs. The frequent annihilation of these defect clusters substantially reduces their life time, to ~ 4 s. Furthermore the life time (in stage 2) of defect clusters in nt specimen is much lower than that in cg specimen (~ 15 s), consistent with the observation of the enhanced defect absorption/interactions with high-density TBs.

The kinetics of defect migration has been evaluated in nt Ag with large average twin spacing (~ 70 nm) via *in situ* studies [42]. In general the global diffusivity of defect clusters (determined by averaging accumulative diffusion distance over a defect's lifetime) in the center

zone of twins (further away from TBs) is higher than those adjacent to TBs. As the defect density in twin interior is greater than those near TBs (but not in the TB affected zones), there are more interactions (migration) among defect clusters in the center of a twinned laminate, and consequently increasing the global diffusivity of these defect clusters. The scenario is slightly different in the current nt Cu. As the average twin spacing of nt Cu is ~ 15 nm, comparable to the width of TB affected zones, ~ 5 nm as observed in irradiated nt Ag [42], the influence of TB affected zones dominates in the current studies. As the migration distances of defect clusters in the TB affected zones are typically small, it is difficult to obtain a reliable measurement of the global diffusivity of defect clusters in nt Cu.

In the early stage of radiation process (stage 1), we observed that 43% of defect clusters nucleated at TBs. Two possible mechanisms might be responsible for this phenomenon. Firstly, a greater amount of interstitials prefer to nucleate at TBs due to collision sequences. $\langle 110 \rangle$ direction in a matrix is parallel to $\langle 411 \rangle$ in a twin, which is not favorable for crowdion formation [60]. Crowdions with $\langle 110 \rangle$ orientation, which do not lie on the $\{111\}$ twinning planes, cannot propagate across TBs. Secondly, the formation energy of $a/3\langle 111 \rangle$ Frank loop is lower on TBs than that in matrix [47]. We use a TB with the stacking sequence of ABCACBA as an example, where the TB is underlined. Inserting an extra $\{111\}$ plane (B in the bracket), the stacking sequence would become ABC(B)ACBA, and we can rewrite it as ABC(B)ACBA, where C is the new TB location. Thus instead of causing stacking faults, we can consider this case as a slight migration of the TB. The frequent migration of TBs would also enhance the interaction of TBs with defect clusters, e.g. SFTs. Note that coalescence and annihilation of the loops would be preferred near TBs, as these loops in twinning planes share the same Burgers vector.

4.3. Elimination of SFTs by TBs and the evolution of TB morphology

Now we examine the interaction between TBs and SFTs in the nt Cu. MD simulations have illustrated possible mechanisms leading to the destruction of an SFT by CTB [39], which was later observed experimentally in Kr ion irradiated nt Ag [41], that is SFTs induced by radiation could be destructed from their bases by interaction with TBs. Here we propose that this mechanism could also be applied to the case where TBs are decorated by SFs.

The HRTEM micrograph in Fig. 10a and the corresponding schematics in Fig. 10b show, after radiation, a partially truncated SFT is sandwiched between TBs, which are decorated by SF ribbons. The base of the SFT adjacent to the SF ribbon is partially removed during radiation. The mechanism of SF-SFT interaction can be explained via schematics in Fig.10c-d. The SFT contains numerous stair-rod dislocations, AB, AC, and BC, with Burgers vectors of $a/6 \langle 110 \rangle$. The arrows indicate the directions of the dislocation lines. When a Shockley partial $a/6[121]$ reaches the SFT from its base plane, it interacts with the three stair-rod dislocations via the following reactions:

$$\frac{a}{6}[1\bar{1}0] + \frac{a}{6}[121] = \frac{a}{6}[211] \quad (\text{along AB}) \quad (5),$$

$$\frac{a}{6}[0\bar{1}1] + \frac{a}{6}[121] = \frac{a}{6}[112] \quad (\text{along AC}) \quad (6),$$

$$\frac{a}{6}[101] + \frac{a}{6}[121] = \frac{a}{3}[111] \quad (\text{along BC}) \quad (7),$$

After reactions, two new Shockley partials, $\frac{a}{6}[211]$ and $\frac{a}{6}[112]$, are generated on the SFT surface plane ABD ($1\bar{1}\bar{1}$) along AB and on ACD ($\bar{1}\bar{1}1$) along AC. The two partials are free

to move on their slip planes, resulting in the unzipping (destruction) of the SFT, shrinkage of the stair-rod dislocation AD, and eventually the collapse of the SFT.

4.4. Creation of ITBs during CTB-dislocation loop interactions

There is a common anticipation that the defect sink strength of grain boundaries scales with the energy of grain boundaries, that is in general high angle grain boundaries are more effective defect sinks than low angle grain boundaries. Consequently it is commonly adopted that CTBs in fcc metals are less effective defect sinks. There are recent experimental evidence derived from **void denuded zones (VDZ)** along grain boundaries that support such a hypothesis [38]. On the other hands, there are scattered evidence that shows that TBs are defect sinks. Segall [61] showed CTBs are biased sinks for vacancies in quenched Al. King and Smith [47] have proposed that CTBs may be sinks for dislocation loops in Al and Cu during *in situ* high-voltage electron radiation. In this study we notice that CTBs interact frequently with dislocation loops and such intensive interactions lead to several consequences.

First, abundant ITBs are generated along CTBs, and in some cases forming curved TBs consisting of a combination of miniscule ITBs and CTBs as observed in irradiated Ag [42]. ITBs are effective defect sinks that accommodate (store) radiation induced defects as the regular high angle grain boundaries do. Additionally the ITBs can effectively transport point defects as MD simulations show defects can easily migrate along certain ITB channels [43]. Meanwhile ITBs contain a high density of mobile partials [62-64], which can actively sweep and engage defect clusters in irradiated twinned metals. Previous studies also show that the interaction of dislocations with CTBs in fcc metals under external stresses can introduce abundant ITBs along

CTBs [65-67]. Furthermore the radiation induced migration of ITBs also arises from the mobility of these Shockley partials.

Second, under external stresses some dislocations (such as Shockley partials, and perfect dislocations) that interact with CTBs [65] may cross-slip on the CTB, leaving mobile Shockley partials on the twinning plane. As mentioned earlier, the abundant Shockley partials on the twinning planes can significantly increase the probability of annihilation of radiation induced defect clusters. Finally the formation of SFs after destruction of SFTs along TBs may also enlarge the TB affected zone and accelerate the removal of defect clusters. These statements are consistent with our experimental observations, which show no dislocation segments, less and smaller defects, and lower defect life time in irradiated nt Cu with an average twin spacing of 15 nm.

It is worth noting that radiation induced local stress could also promote the migration of radiation induced dislocations by confined layer slip, which would increase the odds for perfect dislocation-SFT interactions and subsequent destruction of SFTs.

5. Conclusions

In situ Kr ion irradiation studies were performed on coarse grained Cu and nanotwinned Cu with an average twin spacing of ~ 15 nm. Major findings include the followings: 1) Nanotwinned Cu exhibits enhanced irradiation tolerance in terms of smaller defect size and lower defect density; 2) TBs actively absorb radiation induced defect clusters. 3) TBs destruct SFTs and lead to the formation of SFs along TBs; 4) Incoherent twin boundaries migrate frequently during radiation as these boundaries contain high-density mobile partials; 5) Defect clusters in nanotwinned metals have much shorter life time than those in coarse grained Cu.

These evidence suggests that nanotwins are highly efficient defect sinks that may significantly enhance the radiation tolerance in metallic materials.

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Figure and Table Captions

Table 1. A summary of defect sizes and life time and corresponding doses in stages 1 and 2 for nt and cg Cu.

Fig. 1. Bright field XTEM micrographs showing the evolution of defects during *in situ* Kr ion irradiation of coarse grained (cg) Cu, up to a dose of 1.56 dpa. (a) The as-annealed Cu had a very low density of defect clusters. (b) At 0.01 dpa, the density of defect clusters increased rapidly. (c) Radiation to 0.05 dpa led to a significant increase of defect density and prominent enlargement of the dimension of defect clusters. (d) By 1.56 dpa, a large number of dislocation segments and large defect clusters appeared as marked by arrows in the figure.

Fig. 2. Bright-field X TEM micrographs illustrating the microstructural evolution of the nanotwinned (nt) Cu, irradiated by Kr ions up to 1.56 dpa. (a) The as-deposited nt Cu has an average twin thickness of ~ 15 nm. (b) At 0.1 dpa, defects accumulated moderately both along twin boundaries (TBs) and within twins/matrices. (c) At 0.56 dpa, there is insignificant increase in density of defects compared to that at 0.1 dpa, while TBs were increasingly decorated by stacking faults (SFs). (d) At a higher irradiation dose (1.56 dpa), sporadic dislocation loops appeared and little dislocation segments were observed.

Fig. 3. After irradiation to a dose of 1.56 dpa, higher magnification XTEM and high resolution TEM (HRTEM) images were recorded to examine defects in both nt and cg Cu in detail, along the Cu $\langle 110 \rangle$ zone axis. (a) In cg Cu, a large amount of defect clusters, including SFTs and dislocation segments, were observed. The inset selected area diffraction (SAD) pattern shows that the crystal structure remained single crystal after irradiation. A ring of dislocation segment consisting of large dislocation loops was shown in (a2). (b) In nt Cu at a location with lower twin density (or thicker twins), numerous SFTs were observed. (c) In nt Cu with an average twin

Fig. 5. *In situ* observation of the formation of large defect clusters in cg Cu over a dose of 1.4-1.5 dpa. Dislocation segment 1 interacted with the newly formed segment 2 at 7 s. The two intersecting dislocation segments absorbed peripheral defects to form a larger defect cluster by 31 s. By 33 s, continuous absorption of surrounding defects led to the formation of a large defect cluster. (see Supplementary Video S1 and the playing speed of this video is accelerated by 3 times).

Fig. 7. Comparison of the life time of dislocation loops vs. their distance to TBs in irradiated n-Cu at two radiation stages. In stage 1 (< 0.1 dpa as defined in Fig. 4a), the average life time of defect clusters is 19 s. However, in stage 2, the average life time of defect cluster is 4 s, substantially lower than that in stage 1. For both stages, the life time of defect clusters appears insensitive to their distance to the TBs (varying from 0 to 20 nm).

Fig. 9. The energy of dislocation loops (perfect and Frank loops) and SFTs increases with the number of vacancies contained in a defect cluster. When the radius of a loop is larger than 16 nm, the energy of a perfect loop (E_p) is less than that of a Frank loop (E_F). The energy of SFTs is less than that of both types of loops in the calculated range.

Table 1. A summary of defect sizes and life time and corresponding doses in stages 1 and 2 for nt and cg Cu.

		Average defect size (nm)	Life time/accumulated dose (s/ $\times 10^{-3}$ dpa)
nt Cu	stage 1	5	19 / 8.2
	stage 2	3	4 / 7.9
cg Cu	stage 1	6	15 / 6.5
	stage 2	7	15 / 29.7

Figure 1

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Graphical abstract