

Swift heavy ion irradiation effects in nanocrystalline gold

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Abstract

We have studied the effects of irradiation with energetic ions on defect accumulation in nanocrystalline gold (nano-Au). The specimens of nano-Au foil (3–5 μm thickness) with various grain sizes (23–156 nm) are prepared by the gas deposition method and subsequent thermal annealings. Irradiations of the specimens with 60-MeV ^{12}C ions, 3.54-GeV ^{136}Xe ions or 2.0-MeV electrons are performed at low temperature (below 17–18 K). The defect accumulation behavior is observed by measuring the electrical resistivity change during irradiation. For comparison, irradiation and resistivity measurements are performed on ordinary polycrystalline gold (poly-Au) under similar conditions. Through an analysis of the defect accumulation behavior, the cross-sections for defect annihilation, σ_r , and production, σ_d , in nano-Au are found to increase monotonically as the grain size decreases. These results are considered to be caused by the existence of a large volume fraction of the regions near grain boundaries in nano-Au where the threshold energy for defect production, E_d , may become lower than in poly-Au. For 3.54-GeV ^{136}Xe ion irradiation, in addition to the effect of decrease in E_d , the defect production seems more prominent in nano-Au than in poly-Au. It may suggest that electronic excitation contributes to the defect production effectively in nano-Au.

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1. Introduction

Nanocrystalline materials have typically grain sizes of several tens of nanometers which are much smaller than the conventional polycrystalline materials leading to various novel properties [1,2]. In the present work, we are interested in the radiation resistance of nanocrystalline materials which is expected to be high, since a large volume fraction of grain boundaries may act as effective sinks for irradiation-produced defects. In a recent paper [3], we confirmed

good radiation resistance property of nanocrystalline gold (nano-Au) at 300 K for the first time. For irradiations at 300 K, the produced defects were thermally more unstable in nano-Au than in polycrystalline gold (poly-Au) and therefore, defect accumulation was very small in nano-Au. For low temperature irradiations below ~ 20 K, however, defect accumulation in nano-Au was larger than that in poly-Au, indicating that irradiation-produced defects are easier to be produced in nano-Au than in poly-Au.

In order to clarify the reason for the difference in irradiation behavior for nano-Au and poly-Au, we have studied the dependence of defect accumulation at low temperature on grain size of nano-Au specimen and also on irradiating

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particles by means of in-situ electrical resistivity measurement.

2. Experimental procedure

Specimens of nano-Au were prepared on glass substrates by the gas deposition method [4]. The size of the specimens was $10 \text{ mm} \times 0.5\text{--}1 \text{ mm}$ and $3\text{--}5 \mu\text{m}$ in thickness, which was estimated by gravimetry assuming that nano-Au had the same density as ordinary poly-Au (19.32 g/cm^3). The mean grain size of the specimen was 23 nm estimated from X-ray diffraction pattern [5]. The grain size can be changed by thermal treatment of the specimen. Specimens annealed in a vacuum of $\sim 10^{-4} \text{ Pa}$ for 1 h at 873 K or 1123 K had a grain size of 60 nm and 156 nm , respectively. A specimen was mounted by means of epoxy resin on a copper disk, which was in contact with a cryogenic refrigerator. The specimens of different grain size were irradiated below $17\text{--}18 \text{ K}$ with $60\text{-MeV } ^{12}\text{C}$ ions by using the 20-MV tandem accelerator at JAEA, Tokai Research and Development Center (JAEA-Tokai), 2.0-MeV electrons by using the 3-MV single-ended accelerator in TIARA at JAEA, Takasaki Advanced Radiation Research Institute (JAEA-Takasaki), and $3.54\text{-GeV } ^{136}\text{Xe}$ ions by using the ring cyclotron at RIKEN. All incident particles penetrate the specimen without remarkable energy loss, so that irradiation-produced defects are distributed uniformly in the specimen. We measured the electrical resistivity of the specimen at $7.6\text{--}12 \text{ K}$ by means of a conventional four-probe technique, when irradiation was paused at appropriate fluence intervals. Thus, we could observe particle-fluence dependence of resistivity change. In metals, since resistivity change is proportional to the concentration of irradiation-produced defects, defect accumulation behavior can be obtained for each irradiation. For comparison, a poly-Au foil specimen of $10 \mu\text{m}$ thick (purity 99.9%), which was annealed at 873 K in a vacuum below $3 \times 10^{-5} \text{ Pa}$ for 1 h , was placed adjacent to a nano-Au specimen, and the same particle irradiation and resistivity measurements as mentioned above were performed simultaneously.

3. Results and discussion

Fig. 1 shows the change in the electrical resistivity, $\Delta\rho$, as a function of ion fluence, Φ , i.e. the defect accumulation behavior for $60\text{-MeV } ^{12}\text{C}$ ion irradiation in nano-Au. As a reference, a result for poly-Au is also shown in the figure. For nano-Au, the resistivity change rate, $d(\Delta\rho)/d\Phi$, decreases as the grain size increases, approaching that for poly-Au. In order to evaluate the defect accumulation behavior quantitatively, the following rate equation for describing defect production and annihilation and the solution are adapted as usual;

$$\frac{d(\Delta\rho)}{d\Phi} = \rho_F \frac{dC}{d\Phi} = \rho_F(\sigma_d - \sigma_r C), \quad (1)$$

$$\Delta\rho = \rho_F \frac{\sigma_d}{\sigma_r} \{1 - \exp(-\sigma_r \Phi)\}, \quad (2)$$

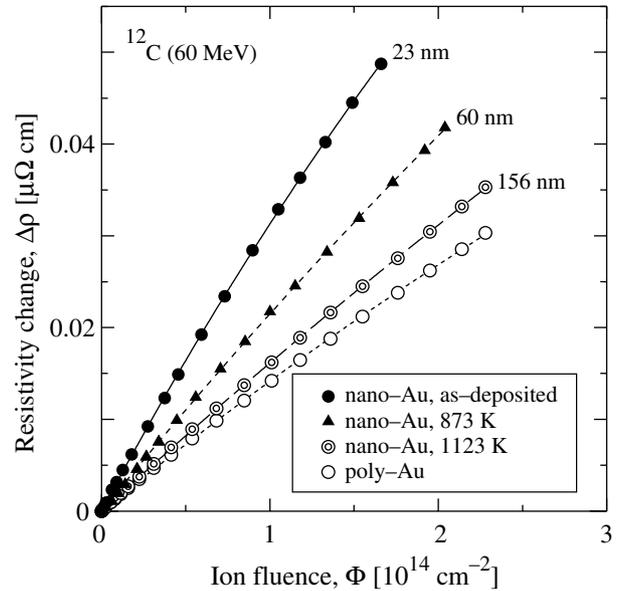


Fig. 1. Defect accumulation behavior for $60\text{-MeV } ^{12}\text{C}$ ion irradiation in nano-Au with grain sizes of 23 nm , 60 nm or 156 nm . A result for poly-Au is also shown.

where ρ_F is the resistivity of unit concentration of defects (Frenkel pairs), C the concentration of defects in the unit of dpa (displacements per atom), σ_d the defect production cross-section, and σ_r the defect annihilation cross-section. The curves shown in Fig. 1 represent the fitting curve of Eq. (2) to the experimental data. In the present work, the value of $\rho_F = 220 \mu\Omega \text{ cm}$ [6] was used for all gold specimens. The derived fit values of σ_r and σ_d are shown as a function of mean grain size in Fig. 2. Both cross-sections increase monotonically with decreasing grain size. This indicates that defects are easier to be annihilated and produced by irradiation in nano-Au specimens with smaller grain size. Regarding the defect annihilation as shown in Fig. 2(a), we have to consider at least the following two possible contributions; (1) low activation energy for migration of defects near grain boundaries, and (2) high probability of annihilation of the defects into grain boundaries as sinks under irradiation. It is noted here that these contributions are consistent with the results of thermal recovery of irradiation-produced defects in nano-Au [3].

In relation to the defect production as shown in Fig. 2(b), on the other hand, we have pointed out in the previous paper [3] that one of the candidates for the cause of the larger defect accumulation rate in nano-Au is the low threshold energy for defect production, E_d , near grain boundaries. We have estimated the value of effective threshold energy, E_d^{eff} , for nano-Au specimen with each grain size under the following assumptions: (a) The increase in σ_d for nano-Au is attributed only to the decrease in E_d , and (b) damage efficiency, ξ , is invariant in both poly-Au and nano-Au for the same kind of irradiation, where ξ is defined as the ratio of the experimental σ_d to the calculated one, σ_d^{cal} , $\xi \equiv \sigma_d / \sigma_d^{\text{cal}}$. The value of σ_d^{cal} , which varies as a function of E_d , was calculated by using

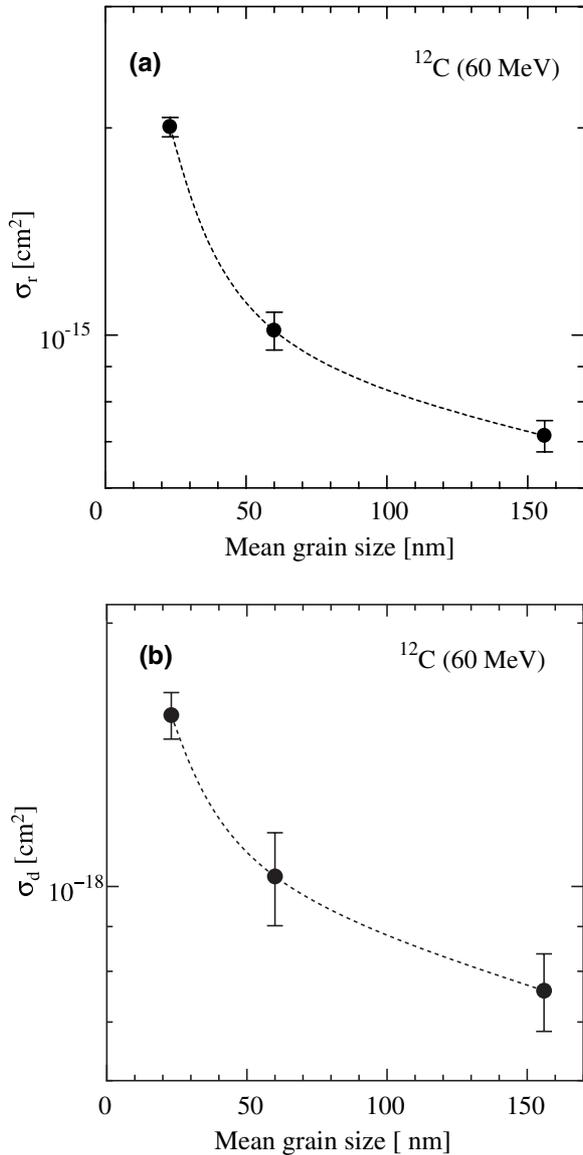


Fig. 2. Mean grain size dependence of cross-sections for (a) defect annihilation, σ_r , and (b) defect production, σ_d , for 60-MeV ^{12}C ion irradiation in nano-Au. These cross-sections are derived from the defect accumulation behavior as shown in Fig. 1. Dotted lines are guides for the eye.

SRIM-2003 code [7] and the value of $E_d = 43$ eV was used for poly-Au [6]. The value of E_d^{eff} for nano-Au was derived as E_d at which ξ coincided with that for poly-Au. Fig. 3 shows the values of E_d^{eff} plotted against the mean grain sizes. As can be seen in the figure, E_d^{eff} decreases monotonically as the grain size decreases. For nano-Au with a grain size of 23 nm, E_d^{eff} becomes about half of the value of E_d for poly-Au. The enhancement in both annihilation and production of defects in nano-Au might possibly be related with the crystal lattice instability due to a large volume fraction of the regions near grain boundaries in nano-Au.

Fig. 4 shows the defect accumulation behavior for irradiations with (a) 2.0-MeV electrons and (b) 3.54-GeV ^{136}Xe ions. The same tendency as the 60-MeV ^{12}C ion irradiation

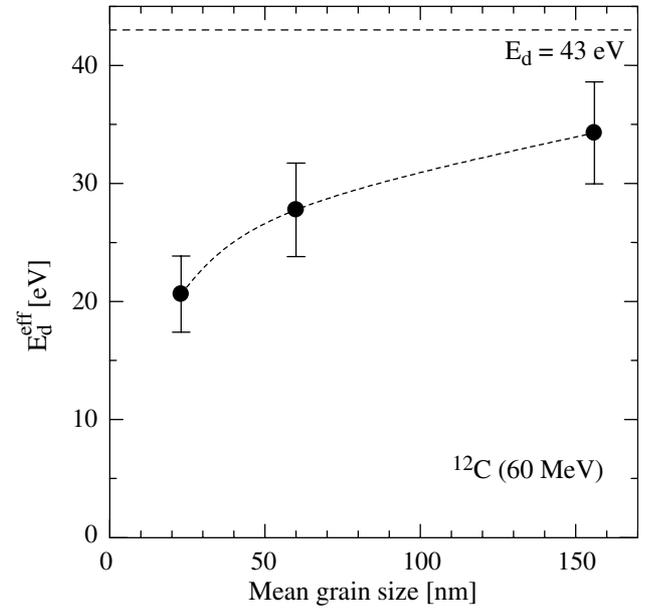


Fig. 3. Mean grain size dependence of effective threshold energy for defect production, E_d^{eff} , for 60-MeV ^{12}C ion irradiation in nano-Au. Dotted line is a guide for the eye. The value of E_d for poly-Au ($E_d = 43$ eV) is also shown as a reference.

(Fig. 1) can be seen in the figure, but the ratio of the resistivity change rate, $d(\Delta\rho)/d\Phi$, in nano-Au to that in poly-Au is different for each irradiation. For example, the average energy of primary knock-on atoms (PKAs) for electron irradiation is comparable to the value of E_d , so that the defect accumulation behavior for electron irradiation reflects sensitively the difference in E_d . Fig. 5 shows the damage efficiency normalized by that for *electron* irradiation in poly-Au, ξ/ξ_c^{poly} , as a function of PKA median energy, $T_{1/2}$, which is the characteristic energy of the PKA energy spectrum [8]. For electron irradiation, the value of σ_d^{cal} was calculated by using Norgett–Robinson–Torrens (NRT) model [9] and the scattering cross-section given by McKinley and Feshbach [10,11]. Assuming that ξ for electron irradiation in nano-Au coincides with ξ_c^{poly} , the value of $E_d^{\text{eff}} \approx 22$ eV is derived for nano-Au. This value is nearly the same as the value shown in Fig. 3 for nano-Au with the grain size of 23 nm. For ^{12}C ion irradiation, the damage efficiency was about 30% of that for electron irradiation, implying that the damage efficiency decreases with increasing $T_{1/2}$. The same kind of $T_{1/2}$ dependence of the damage efficiency has been reported also for many kinds of metals [12–15], which indicates that the defect production is governed by the elastic interactions between the incident particle and the target atoms. For ^{136}Xe ion irradiation, however, the damage efficiency deviates from this tendency, especially in nano-Au. This result suggests the enhancement of the defect production due to the high electronic excitation. In fact, defects can be produced through high-density electronic excitation for copper and silver [14], which are the same I-b elements as gold. The larger value of ξ in nano-Au than in poly-Au might be explained as a

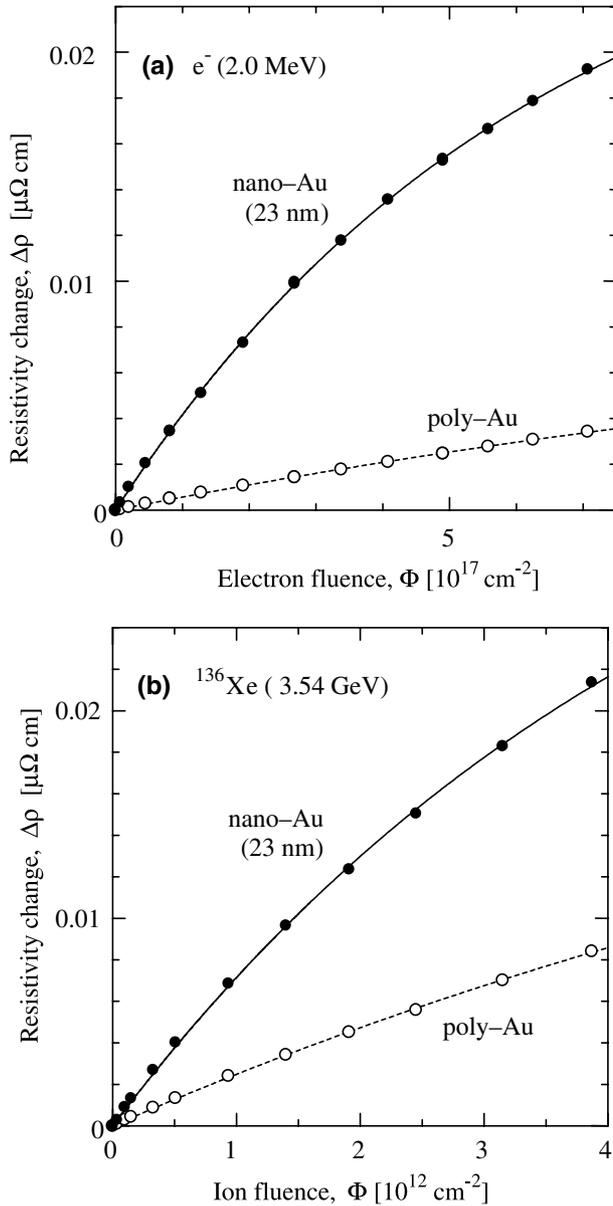


Fig. 4. Defect accumulation behavior for irradiations in nano-Au and poly-Au with (a) 2.0-MeV electrons and (b) 3.54-GeV ^{136}Xe ions.

result of the confinement of the transferred energy through electronic excitation within a crystal grain. To confirm whether there exists the electronic excitation effect, systematic investigation of ion irradiation behavior in wide mass and energy ranges is indispensable.

4. Summary

Defect accumulation has been studied in nano-Au irradiated with energetic particles. Through an analysis, cross-sections for defect annihilation, σ_r , and production, σ_d , in nano-Au are found to increase monotonically as the grain size decreases. These results show that defects are easier to be annihilated and produced by irradiation in nano-Au with smaller grain size. Moreover, assuming

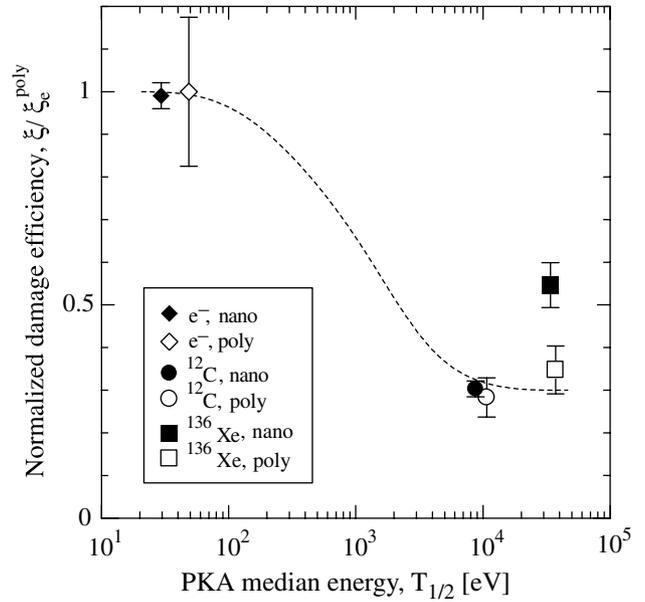


Fig. 5. Normalized damage efficiency, ξ/ξ_c^{poly} , plotted against PKA median energy, $T_{1/2}$, for irradiations with 2.0-MeV electrons, 60-MeV ^{12}C ions and 3.54-GeV ^{136}Xe ions in nano-Au and poly-Au. The values we used as E_d for poly-Au and E_d^{eff} for nano-Au are 43 eV and 22 eV, respectively. Dotted line is a guide for the eye.

that the increase in σ_d is attributed only to the decrease in E_d , the value of effective E_d , E_d^{eff} , for nano-Au is estimated to be about half of the value of E_d for poly-Au. The enhancement in both annihilation and production of defects in nano-Au might be related to the crystal lattice instability in nano-Au, which has a large volume fraction of the regions near grain boundaries. For 3.54-GeV ^{136}Xe ion irradiation, in addition to the effect of decrease in E_d , the amount of the defect production seems to be larger in nano-Au than in poly-Au. The present result implies that electronic excitations effectively contribute to the defect production in nano-Au.

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