Anomalous Ion Accelerated Bulk Diffusion of Interstitial Nitrogen

Gintautas Abrasonis* and Wolfhard Möller
Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, PF-510119, 01314 Dresden, Germany

Xin Xin Ma
School of Materials Science and Engineering, Harbin Institute of Technology, 150001 Harbin, China

(Received 19 August 2005; published 13 February 2006)

Interstitial N diffusion under low energy (~700 eV) Ar^+ bombardment at 673 K in ion beam nitrided austenitic stainless steel is investigated. Ar^+ ion bombardment increases the N mobility in depths far beyond the ion penetration depth, resulting in an increased broadening of the N depth profile as a function of Ar^+ flux. This effect cannot be explained by any established mechanism of radiation-enhanced diffusion. An explanation based on quasiparticle-enhanced mobility is proposed.

DOI: 10.1103/PhysRevLett.96.065901 PACS numbers: 66.30.Jt, 61.80.Jh, 63.20.Ry

Transport phenomena in ion-irradiated solids can be classified into athermal collisional processes such as recoil implantation and cascade mixing, and processes which require thermal activation such as purely thermal diffusion or radiation-enhanced diffusion [1]. The athermal processes act in a depth range which is affected by the slowing down of the ions and relocation of atoms due to single or multiple knock-on events. In contrast, the present Letter reports on the existence of an ion induced athermal process which is effective to a depth being several orders of magnitude larger than the dimensions of the collision cascade. N diffusion in the austenitic stainless steel (ASS) under Ar ion bombardment is studied. Because of the broad application domain of ASS, a large amount of information is available, such as reliable experimental information on point defect diffusion and extensive studies of the modeling of ion nitriding. For the present system of N implanted into ASS, the diffusional formation of a highly metastable supersaturated interstitial N solid solution at temperatures around 673 K is well established [2–6]. However, it was shown that the N diffusivity depends on the N ion flux [7–10] for which no satisfactory explanation could be given. In the present work, an experiment has been designed to clearly establish the effect of ion bombardment on deep diffusion. An interpretation is attempted on the basis of ion irradiation created quasiparticles that can propagate over long distances in the 3D lattice interacting with the interstitial atoms and affecting their mobility.

Three mm thick discs, 10 mm in diameter, were cut from commercial ASS AISI 316L rods (Cr concentration ~18.5 at. %). Mechanical polishing produced a final roughness of 0.01 μm. Ar and N ion bombardment was performed using a Kaufman-type ion source of 3 cm diameter. The ion current density was measured using a Faraday cup. Samples were heated in vacuum up to ~573 K using a boron nitride heater and precleaned for 15 min using a 1 keV Ar^+ beam with a flux of 3.1 ions $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$. During the precleaning stage the sample temperature T measured by a thermocouple inserted through a hole in the side of the sample reached the steady state at ~673 K. The Ar^+ beam was then gradually changed to a pure N ion beam, resulting in ion beam nitriding for 40 min with 1 keV N ions at 3.1 ions $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$. The base pressure was 3–4 $\times 10^{-4}$ Pa, rising to 10^{-2} Pa during implantation.

In order to investigate the N diffusion under ion bombardment, after nitriding the samples were immediately (after ~1.5 min) irradiated by Ar^+ at a constant temperature of 673 K. The Ar^+ energy was fixed at 700 eV while the Ar^+ flux was different for each sample: 1.3×10^{15}, 2.5×10^{15}, and 3.8×10^{15} ions $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$ (I_1–I_3, respectively). T decreased by ~20 K while switching the ion beam from N to Ar and reached a steady-state value of 673 K after ~4–5 min. The Ar^+ penetration depth calculated using SRIM 2003 [11] is ~1–2 nm. In view of significant Ar^+ induced sputtering, the ion fluence was held constant at 4.5×10^{18} ions cm^{-2} in order to produce the same amount of sputtered material for all samples. Thus the samples were bombarded during 60, 30, and 20 min for I_1–I_3, respectively. TRIDYN [12] simulations show that Ar^+ bombardment of N containing ASS produces a N depleted near-surface layer, while the sputtering yield of matrix atoms approaches that of the non-nitrided steel. Accordingly, a sputtered depth of ~0.55 μm was measured for the above fluence using surface profilometry on a non-nitrided sample.

X-ray diffraction revealed the modified layer structure to be composed of only "expanded" austenite in both as-nitrided and Ar^+ postirradiated samples, with no evidence of nitride formation. Quantitative N depth profiles were determined by nuclear reaction analysis (for details, see Ref. [10]). Figures 1(a)–1(d) show the N depth profiles without and with Ar^+ irradiation post-treatment. The N profile of the as-nitrided sample can be depicted by an initial quasilinear decrease changing to a sharp leading edge at a depth of ~1 μm. The N concentration at this point is ~15 at. %, which is equal to the Cr concentration taking into account the renormalization of the nominal ASS concentrations due to the N addition. The shape of the N depth profile is consistent with the trapping-

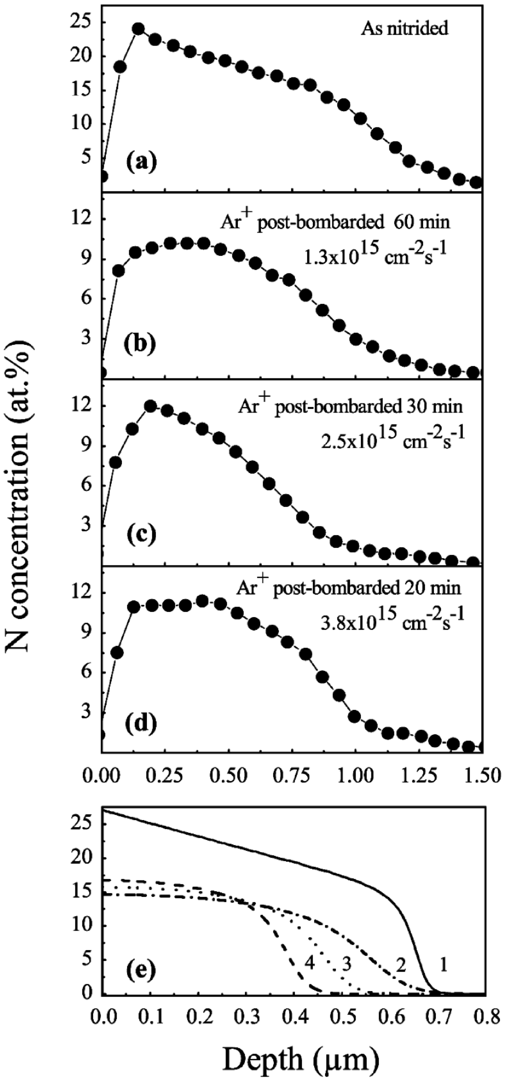

FIG. 1. Experimental (a)–(d) and calculated (e) (using the TD model) N depth profiles in ASS. Experimental profiles correspond to N depth distributions after ion beam nitriding (a) and postnitriding irradiation using an Ar$^+$ beam with ion fluxes 1.3×10^{15} (b), 2.5×10^{15} (c), and 3.8×10^{15} (d) ions s^{-1} cm^{-2}. Calculated profiles (e) correspond to N depth distributions after nitriding (curve 1) and subsequent N diffusion under simultaneous sputtering induced surface erosion for different diffusion constants equal to 6.0, 3.0, and 1.5×10^{-12} cm^2 s^{-1} (curves 2–4, respectively). The as-nitrided profile was calculated for $t =$ 30 min assuming an N diffusion coefficient of $D = 3.0 \times 10^{-12}$ cm^2 s^{-1}, a detrapping energy 0.35 eV, a sputtering induced surface recession velocity of $V_S = 1.7 \times 10^{-8}$ cm s^{-1}, and an incoming N flux of 4.84×10^{15} cm^{-2} s^{-1} (according to the distribution of atomic and molecular ions in the beam). The Ar$^+$ post-treatment was simulated assuming $V_S = 4.4 \times 10^{-8}$ cm s^{-1} and $t = 15$ min.

detrapping (TD) model [13], according to which the Cr atoms trap mobile N atoms by forming a chemical bond. This significantly slows down N diffusion in the regions where the N concentration is below the Cr concentration, resulting in the observed profile shape.

In the following, the depth profiles after Ar$^+$ postirradiation are understood in terms of a sputtering/diffusion balance, where sputtering reduces the integrated N content and the width of the profiles, whereas diffusion broadens the profiles and thereby results in an increased integral N amount. The N distribution profiles exhibit a plateau near the surface followed by a slow decrease in N concentration. The N plateau concentration is slightly dependent on Ar$^+$ flux and increases from ∼10 to ∼12 at. % when the Ar$^+$ flux increases from I_1 to I_3, respectively. Additionally, the N concentration falls below that of Cr, which indicates that N is mainly in the trapped state. It can be seen that after annealing with moderate Ar$^+$ bombardment, the profile shape changes from the concave characteristic for the leading edge of the as-nitrided sample to a convex characteristics of postnitriding annealed samples [10]. When the Ar$^+$ flux is doubled (diffusion time t is half), the N penetration depth decrease, which is consistent with conventional diffusion. However, when the Ar$^+$ flux is tripled in comparison to the lowest one (t is reduced by a factor of 3) the N penetration depth is again higher and similar to that obtained at the longest time, which clearly indicates an additional influence of ion flux on the N transport.

The profile shape after Ar$^+$ post-treatment is qualitatively consistent with the TD model, as demonstrated in Fig. 1(e) under the assumption of three different diffusion coefficients D (for details of the calculation, see Refs. [10,13]). It is confirmed that sputtering induces a significant N loss, while diffusion results in flattening and broadening of the depth profiles, with higher D yielding higher N penetration depths and lower N near-surface concentrations. Additional simulations show that doubling (or tripling) V_S and D while reducing t by a factor of 2 (or 3) results in identical N depth profiles. In comparison to the above, this indicates that the diffusivity increases by a factor of about 3 when the Ar$^+$ flux increases from I_1 to I_3 [see Figs. 1(b) and 1(d)]. Thus, although being unable to account for the underlying mechanisms, the TD model provides a quantitative estimate through the assumption of a diffusion coefficient which depends on the ion flux.

This is consistent with previous findings that the N diffusivity during ion nitriding of ASS increases with the N ion flux [7,10]. This also underlines that the observed phenomenon is related to ion irradiation but not to the irradiating species. Also, the observed increase of the nitriding depth with ion energy [7] indicates an irradiation-induced enhancement of diffusion. Further evidence of a yet unidentified transport mechanism has been established for ion nitriding of ASS single crystals, which showed a significant dependence of the nitriding depth on the crystalline orientation [6] (see also Ref. [3]), although the diffusion in a cubic material is expected to be isotropic.

Before tentatively proposing a mechanism of the observed effect, we wish to discuss other processes which would be consistent with present perception. Although unlikely, an influence of the Ar$^+$ ion flux on the sputtering has been ruled out by demonstrating that identical N depth profiles are obtained at temperatures between 373 and 473 K at identical fluence but different fluxes. Vacancy or multivacancy mediated diffusion cannot explain the observations as N diffusion has been found to be faster than that of vacancylike defects during ion beam nitriding of ASS [14]. Furthermore, the dynamic vacancy concentration for the present experimental situation has been calculated using simple diffusion theory [15] with the vacancy diffusion constant given by Pokor *et al.* [16] and a vacancy source distribution obtained from SRIM 2003. Assuming a sink at the surface, an almost constant vacancy concentration profile is obtained at the above time of 30 min and the corresponding flux, with a relative concentration close to 10^{-3} which is much smaller than the N concentration. The diffusion of self-interstitials is much faster [16], resulting in an even much lower concentration. Furthermore, a significant self-diffusion would result in the precipitation of CrN [2], which is not observed. Thus, any influence of radiation-induced diffusion can be ruled out with a high level of confidence. Stress-mediated or concentration dependent [17] diffusion would be in contradiction with the similar N depth distributions obtained at different diffusion times for different N ion fluxes [10]. Any thermal acceleration of diffusion by the ion irradiation can also be excluded. An assumed temperature increase of 10 K, which is far above the precision of the experimental control, would increase the diffusion coefficient by a factor of 1.4, which is significantly below the variation shown in Fig. 1. Further, the calculation of the hemispherical thermal spike induced by each ion shows a dissipation to a transient heating of less than 1 mK already at a depth of 0.1 μm, so that any resulting effects can be excluded. Diffusion of lower dimensionality (grain boundaries, dislocations) does not explain the present results either because the N distribution and defect concentration after nitriding is similar for all samples. Thus, from conventional pictures no diffusion acceleration can be expected. Nevertheless, the process appears to be diffusionlike because of the good agreement between experimental and calculated N depth profiles [10,13].

It is well known that if the energy transferred from the ion/recoiled atom to the target atoms is not sufficient to create a Frenkel pair (~30 eV), this energy is dissipated into lattice vibrational excitations. If the transferred energy is of the order of thermal energies (~0.01 eV), the atomic displacement is in the range of linear restoring interatomic forces, and the energy will be dissipated at short distances. This type of lattice excitation cannot influence the atomic diffusion far beyond the ion penetration depth. When the transferred energy is in an intermediate region, atoms will experience large displacements from their equilibrium positions, while remaining at their original lattice sites. Propagation of the corresponding lattice vibrations may be governed by nonlinear forces. As described in the literature, this may result in the formation of a vibrational particlelike soliton which can propagate distances well beyond the dimensions of the collision cascade [18,19].

It was shown theoretically that the presence of the surrounding lattice prevents the propagation of Toda-like solitons [18] but allows breatherlike solitons [or so-called discrete breathers (DB)] to propagate along atomic chains [20]. According to molecular dynamic (MD) simulations, DBs are highly anharmonic longitudinal vibrations, being sharply localized on just a few sites in the longitudional direction and practically across one atomic distance in the transverse direction. Within this oscillation envelope the particles execute antiphase or optical type oscillations [20]. The highly localized excitations on the atomic scale were observed in a quasi-one-dimensional antiferromagnet [21] and atomic lattices [22,23]. Additionally, MD simulations show that giving an impulse, as when an atomic collision takes place, to just one atom is enough to create the moving DB [20]. Following this we speculate that DB's might be created by N or Ar ions during ion nitriding and in the present experiment, leave the collision cascade region, and move away from the surface and enhance diffusion at large depths. It has been shown that vacancy migration can be induced by a DB [24]. In analogy, we expect that a DB can also accelerate the diffusion of interstitial atoms, in particular, as the activation energy of interstitial migration is generally smaller than that of vacancy migration. Because of the high amplitude antiphase vibration, diffusional jumps of N atoms might be assisted by DB's in their close vicinity. In this picture, thermal vibrations and DB's would act synergistically. An independent athermal DB mechanism would result in a constant additional profile broadening at constant ion fluence, and, consequently, in a continuous decrease of the profile width at increasing flux which is in contrast to the findings of Fig. 1. Therefore, one might tentatively write the diffusion coefficient as

$$D = D_0 \exp\left(-\frac{E}{kT}\right) \exp\left(\frac{\alpha I}{kT}\right) = D_{\mathrm{th}} \exp\left(\frac{\alpha I}{kT}\right), \quad (1)$$

with the conventional thermal diffusion coefficient D_{th} given by the preexponential factor D_0 and the activation energy E, and an enhancement term which depends exponentially on the ion flux I, α being a positive constant.

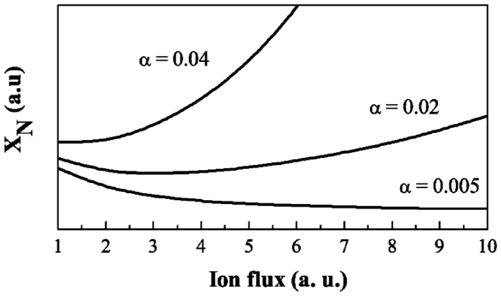

FIG. 2. N penetration depth $X_N \sim \sqrt{Dt}$ as a function of surface irradiating ion flux I for fixed ion fluence and different flux susceptibility factors α (see text). Diffusion preexponential factor D_0, thermal activation energy E, and T were 10^{-3} cm^2 s^{-1}, 1.1 eV, and 673 K, respectively.

Equation (1) can also be interpreted as an effective coefficient of thermal diffusion, the activation energy of which decreases linearly with the ion flux due to the lattice distortions induced by DB's. From Eq. (1), Fig. 2 presents the mean diffusional depth X_N as a function of I for fixed ion fluence (identical sputtered depth) and different α values, assuming the simplest model of "free" N diffusion (i.e., $X_N \sim \sqrt{Dt}$). Three regimes can be identified: (1) low α values—X_N decreases when I increases (ion enhancement is too small as to compensate for shorter diffusion times); (2) high α values—X_N increases when I increases (ion enhancement produces thicker layers despite lower t); (3) intermediate values—X_N decreases, reaching a minimum before increasing. According to this simplified picture, the above results should be related to the intermediate regime.

It can presently only be speculated which implantation conditions may favor the DB generation. They may result from knock-on events which generate recoils with a direction close to low-indexed crystallographic directions, and a transferred energy which is large compared to thermal energies but smaller than the lattice binding energy of a few eV. During the energy dissipation of the collision cascade, such collisions will occur more frequently as the nuclear stopping increases. For Ar^+ bombardment of ASS, nuclear stopping peaks at around 35 keV, so one may anticipate an increase of the effect at higher energies, in qualitative agreement with the increased nitriding depth at increased ion energy [7] as mentioned above. On the other hand, higher energies promote dynamic disorder in the cascade, which may impede the launching of DBs. These questions will be addressed in future experimental and MD computer simulation studies.

In summary, it was observed that low energy (700 eV) Ar^+ irradiation significantly increases the interstitial N mobility in ASS at depths well beyond the ion penetration depth. It manifests itself as the increased broadening of the N depth profile as a function of Ar^+ flux. The observed effect cannot be explained by any established mechanisms of radiation-enhanced diffusion. Therefore, a possible mechanism is proposed involving nonlinear vibrational excitations such as discrete breathers, which might explain the dependence of the diffusional depth on the ion flux and on the crystalline direction in cubic crystals, which were hitherto obscure. This mechanism may be more general and applicable to other processes involving atomic mobility in ion-irradiated materials. The degree to which these processes are influenced by ion bombardment may depend on the type and energy of impinging energetic particles, the composition and microstructure of irradiated material, and the stability of the quasiparticles.

We are grateful for financial support of the Saxonian government and Harbin Institute of Technology Internationalizing Foundation, China. In addition we would like to thank Professor Claude Templier and Professor Jean Paul Rivière from Laboratoire de Métallurgie Physique, Poitiers, France, for providing the austenitic stainless steel samples.

---

*Electronic address: g.abrasonis@fz-rossendorf.de

[1] P. Sigmund and N. Q. Lam, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **43**, 255 (1993), and references therein.

[2] D. L. Williamson, O. Ozturk, R. Wei, and P. J. Wilbur, Surf. Coat. Technol. **65**, 15 (1994).

[3] O. Öztürk and D. L. Williamson, J. Appl. Phys. **77**, 3839 (1995).

[4] S. Grigull and S. Parascandola, J. Appl. Phys. **88**, 6925 (2000).

[5] C. Blawert, H. Kalvelage, B. L. Mordike, G. A. Collins, K. T. Short, Y. Jirásková, and O. Schneeweiss, Surf. Coat. Technol. **136**, 181 (2001).

[6] G. Abrasonis, J. P. Rivière, C. Templier, A. Declémy, L. Pranevicius, and X. Milhet, J. Appl. Phys. **97**, 083531 (2005).

[7] D. L. Williamson, J. A. Davis, P. J. Wilbur, J. J. Vajo, R. Wei, and J. N. Matossian, Nucl. Instrum. Methods Phys. Res., Sect. B **127–128**, 930 (1997).

[8] C. Blawert, B. L. Mordike, G. A. Collins, K. T. Short, and J. Tendys, Surf. Coat. Technol. **103–104**, 240 (1998).

[9] N. Tsubouchi, Y. Mokuno, A. Chayahara, and Y. Horino, Surf. Coat. Technol. **196**, 271 (2005).

[10] G. Abrasonis, J. P. Rivière, C. Templier, L. Pranevičius, and N. P. Barradas, J. Appl. Phys. **97**, 124906 (2005).

[11] J. F. Ziegler and J. P. Biersack, Computer code SRIM 2003 program package, http://www.srim.org

[12] W. Möller, W. Eckstein, and J. P. Biersack, Comput. Phys. Commun. **51**, 355 (1988).

[13] S. Parascandola, W. Möller, and D. L. Williamson, Appl. Phys. Lett. **76**, 2194 (2000).

[14] W. Anwand, S. Parascandola, E. Richter, G. Brauer, P. G. Coleman, and W. Möller, Nucl. Instrum. Methods Phys. Res., Sect. B **136–138**, 768 (1998).

[15] J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, 1985).

[16] C. Pokor, Y. Brechet, P. Dubuisson, J.-P. Massoud, and A. Barbu, J. Nucl. Mater. **326**, 19 (2004).

[17] S. Mändl and B. Rauschenbach, J. Appl. Phys. **91**, 9737 (2002).

[18] Y. V. Martynenko and P. G. Moscovkin, Radiat. Eff. Defects Solids **117**, 321 (1991).

[19] F. M. Russell and D. R. Collins, Nucl. Instrum. Methods Phys. Res., Sect. B **105**, 30 (1995).

[20] J. L. Marín, J. C. Eilbeck, and F. M. Russell, in *Nonlinear Science at the Dawn of the 21st Century*, edited by P. L. Christiansen, M. P. Sorensen, and A. C. Scott (Springer, Berlin, 2000), p. 293.

[21] M. Sato and A. J. Sievers, Nature (London) **432**, 486 (2004).

[22] B. I. Swanson, J. A. Brozik, S. P. Love, G. F. Strouse, A. P. Shreve, A. R. Bishop, W.-Z. Wang, and M. I. Salkola, Phys. Rev. Lett. **82**, 3288 (1999).

[23] T. Markovich, E. Polturak, J. Bossy, and E. Farhi, Phys. Rev. Lett. **88**, 195301 (2002).

[24] J. Cuevas, C. Katerji, J. F. R. Archilla, J. C. Eilbeck, and F. M. Russell, Phys. Lett. A **315**, 364 (2003).