Atomic defects in hexagonal tungsten carbide studied by positron annihilation

A. A. Rempel*
Universität Stuttgart, Institut für Theoretische und Angewandte Physik, D-70550 Stuttgart, Germany

R. Würschum
Universität Stuttgart, Institut für Theoretische und Angewandte Physik, D-70550 Stuttgart, Germany
and Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Postfach 3640, D-76021 Karlsruhe, Germany

H.-E. Schaefer
Universität Stuttgart, Institut für Theoretische und Angewandte Physik, D-70550 Stuttgart, Germany
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Vacancies on the two sublattices of hexagonal tungsten carbide were identified by means of positron lifetime studies after irradiation with electron of various energies. In the as-prepared state two predominant positron lifetime components occur indicating positron annihilation in the free state with a lifetime $\tau_f = 124 \pm 10$ ps according to the simple trapping model and positron trapping and annihilation in metal vacancies ($\tau_{V_W} = 175 \pm 20$ ps) of low concentration. By means of low-energy electron irradiation at 1 MeV with an electron dose of 1.8×10^{23} m^{-2} exclusively carbon vacancies are introduced giving rise to saturation trapping and annihilation of positrons at carbon vacancies with a low lifetime of $\tau_{V_C} = 136 \pm 3$ ps. The isochronal annealing of irradiation induced vacancies reveals two annealing stages at 800 and 1200 K, which are ascribed to the annealing of carbon vacancies and the dissolving of small carbon vacancy clusters.

I. INTRODUCTION

Hexagonal tungsten carbide (WC) is of practical interest for engineering applications as a high-melting refractory material ($T_{melt.} = 3050$ K) with high mechanical stability,[1,2] as hard metal in combination with a cobalt binder, and due to its high catalytic activity which is similar to that of Pt.[3] In addition, WC is of theoretical interest due to its chemical bonding which represents a mixture of covalent, ionic, and metallic components. A number of papers (for the literature, see Ref. 4) has been devoted to theoretical studies of the electronic structure of hexagonal tungsten carbide, providing evidence that the conductivity is of purely metallic nature and that the electronic density of states exhibits a minimum near the Fermi surface.

Data on the characteristics of point defects of WC which are of great interest for the understanding of self-diffusion processes, mechanical strength, brittleness, and plasticity are scarcely available. In contrast to the carbides of the group IV and V transition metals,[5,6] hexagonal tungsten carbide can be synthesized with a stoichiometric composition and a relatively low concentration of atomic defects on the metal and the carbon sublattices. The low defect concentration is reflected in a low electrical resistivity $\rho(4.2\ \mathrm{K}) = 0.45\ \mu\Omega$ with a high residual resistivity ratio $\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K}) = 35$ measured on high-quality single crystal with a fully stoichiometric composition.[7] A low defect concentration is also supported by recent positron annihilation studies[8,9] of WC where a short positron lifetime component in the range of 100 ps indicated partial positron annihilation from the free state. Owing to the high sensitivity of the technique to vacancy-type defects[10] this is feasible only for atomic vacancy concentrations below 10^{-4}.

Recent first-principle calculations of the positron lifetime[11] which were carried out for virtual $B1$-WC, yield for the free state a low value of 95 ps supporting the values observed experimentally (see above) or calculated[9] on the basis of an empirical model.[12] According to the *ab initio* calculations[11] the positron lifetime $\tau_{V_C} = 116$ ps in a carbon vacancy is only slightly higher than the free positron lifetime, whereas the lifetime of positrons in a metal vacancy with 161 ps is substantially higher.

Based on these results the present work aims at a more detailed experimental characterization of vacancies on the two sublattices of WC. For this purpose positron lifetime measurements were performed after irradiation with electrons of various energies. As demonstrated earlier in the cases of GaAs (Ref. 13) or SiC (Ref. 14), positron lifetime measurements in binary crystalline compounds after low-temperature electron irradiation near or well above the threshold of atomic displacement may provide specific information on vacancy-type defects on the two sublattices. Hence they may contribute to the assessment of thermal defects at high temperatures or of structural vacancies. The stability of the defects in WC was studied by means of isochronal annealing after electron irradiation.

II. EXPERIMENT

Positron lifetime studies were performed on hexagonal tungsten carbide (WC) powder (WC-PWD), on sintered polycrystalline WC (WC-SNT) and on a composite of WC embedded in a Co binder (WC-HM). Crystallite sizes of $1-3$ μm were determined for the WC powder, whereas in the WC sintered at 2100 K for 4 h in vacuum and subsequently cooled within 5 h (WC-SNT1, WC-SNT2) a crystallite size of 1 to 10 μm was found. The WC hard metal (WC-HM) was synthesized with 6 wt % of Co by liquid phase sintering at 1670 K.

The chemical composition of the specimens was deter-

TABLE I. Positron lifetime components τ_i with relative intensities I_i ($i=0-2, I_2=1-I_1-I_0$), mean positron lifetime $\overline{\tau}$, and free positron lifetime τ_f according to simple two-state trapping model in tungsten carbide specimens prior to irradiation (as-prepared). WC-PWD, powder of WC; WC-SNT1 and WC-SNT2, sintered powders of WC; WC-HM, hard metal of WC with Co binder.

Specimen	τ_0 [ps]	I_0 [%]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	$\overline{\tau}$ [ps]	τ_f [ps]
WC-PWD	95±1	49±1	158±2	47±1	490±10	140±2	122±4
WC-SNT1	102±1	56.5±2	179±2	41.1±1	540±20	144±2	127±5
WC-SNT2	100±1	65.2±2	192±2	32.2±1	550±20	141±2	121±5
WC-HM	104±1	53.8±1	190±2	43.9±1	572±10	152±2	133±4

mined by energy dispersive analysis of x rays (EDX) within an uncertainty of 0.5 at. % for both heavy and light elements. No impurities exceeding these uncertainty limits could be detected. By means of x-ray diffraction a hexagonal structure with the space group $P\overline{6}m2$ and with the lattice parameters $a=0.2906$ and $c=0.2837$ nm were determined without the detection of any other phase.

The positron lifetime was measured with a fast-slow $\gamma\gamma$ spectrometer with a time resolution of 260 ps (FWHM, full width at half maximum) using a ^{22}NaCl positron emitter (1–2 MBq) on a 0.8-μm-thin Al foil stacked between two identical specimen platelets. The positron lifetime components τ_i with relative intensities I_i were numerically determined from spectra with a statistical accuracy of $(2-7)\times10^6$ coincidences by means of standard techniques considering a source correction.[15]

The electron irradiations with low- (1.0 MeV) and high-energy (2.5 MeV) electrons and doses of 1.8×10^{23} and 1.2×10^{22} m^{-2}, respectively, were performed at the Dynamitron accelerator of Stuttgart University (see Ref. 16). The maximum specimen temperature was 200 or 80 K during low- and high-energy irradiation, respectively.

Measurements after isochronal annealing from ambient temperature to 1300 K with 100 K step (annealing time 1 h) were performed on the irradiated WC composite (WC-HM) under high vacuum of a pressure lower than 10^{-4} Pa.

III. RESULTS AND DISCUSSION

In the WC powder and the sintered WC specimens similar values of the mean positron lifetime $\overline{\tau}=140-144$ ps occur in the as-prepared state whereas in the WC hard-metal composite (WC-HM) $\overline{\tau}$ is slightly higher (Table I). These values of $\overline{\tau}$ are significantly lower than the mean positron lifetime $\overline{\tau}=155-176$ ps observed in the group IV and group V transition-metal carbides (see Refs. 12 and 17).

Positron lifetime spectroscopy reveals two dominant components with the lifetimes τ_0 and τ_1 and an additional weak component τ_2 in the as-prepared WC specimens (Table I). We attribute τ_0 to the positron residence time in the undisturbed lattice and the lifetimes τ_1 and τ_2 to positron trapping and annihilation at defects. The absence of the short-lived component τ_C supports the earlier findings[8,9] that WC can be prepared with a low concentration of vacancy-type defects. The free positron lifetime $\tau_f=1/(I_0/\tau_0+I_1/\tau_1+I_2/\tau_2)=121-127$ ps (see Table I) deduced from the positron lifetime components τ_1 according to the simple trapping model[10] appears to be slightly higher than the theoretical value $\tau_f=95$ ps (see above, Ref. 11). Taking into account the positron lifetime 161 ps calculated for tungsten vacancy[11] the positron lifetime component $\tau_1=158-192$ ps (Table I) is ascribed to positron trapping and annihilation at mono- or divacancies on the metal sublattice. The positron lifetime τ_2 (Table I) with weak intensity may originate from positrons trapped at nanovoids inside the crystallites. Positron trapping at grain boundaries of the polycrystalline WC specimens is considered to be negligible due to the crystallite size of a few micrometers which is much larger than the positron diffusion length $D_f\approx100$ nm (Refs. 18 and 19) in defect-free crystals.

After irradiation with electrons of the energy $E_1=1.0$ MeV a single-component spectrum with a positron lifetime $\overline{\tau}=\tau_1=135-137$ ps *lower* than that before irradiation occurs (Table II, Fig. 1). This most striking feature of the present studies is in contrast to the irradiation of initially defect-free metals,[16] semiconductors,[13,14,17] or stoichiometric metal oxides[20] where the positron lifetime increases due to radiation-induced vacancies. After irradiation with electrons of higher energy ($E_2=2.5$ MeV) the mean positron lifetime is higher than after low-energy irradiation and similar to the value measured prior to irradiation (Table II).

For an assessment of the dependence on electron energy the types and concentrations of defects generated by electron

TABLE II. Positron lifetime components τ_1 and τ_2 with relative intensity I_2 ($I_1=1-I_2$) and mean positron lifetime $\overline{\tau}$ in electron-irradiated tungsten carbides (specimens WC-SNT1, WC-HM). The irradiation was performed with the electron energies $E_1=1.0$ MeV and $E_2=2.5$ MeV and the doses $\Phi_1=1.8\times10^{23}$ and $\Phi_2=1.2\times10^{22}$ m^{-2} at the temperature T_{irr}.

Specimen	Energy, dose	T_{irr} [K]	τ_1 [ps]	τ_2	I_2 [%]	$\overline{\tau}$ [ps]
WC-SNT1	E_1, Φ_1	200	135±1		0	135±1
WC-HM	E_1, Φ_1	200	136±1		0	136±1
WC-HM	E_2, Φ_2	80	137±2	400±40	3.8±1	147±2

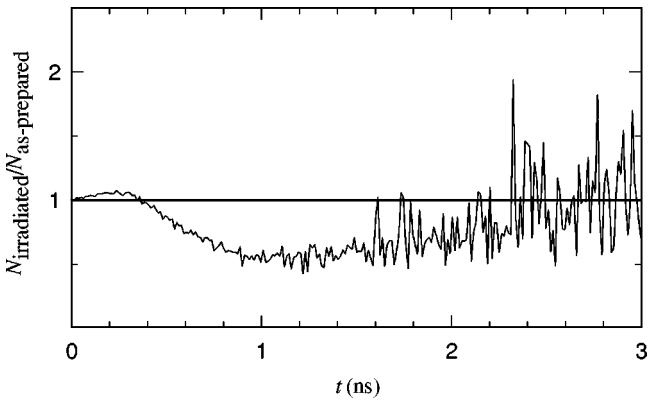

FIG. 1. Ratio of the number of counts in the positron lifetime spectra measured on tungsten carbide before ($N_{as\text{-}prepared}$) and after electron irradiation at 200 K ($N_{irradiated}$) with an electron energy of $E_1=1.0$ MeV and electron dose of $\Phi_1=1.8\times10^{23}$ m^{-2} versus time t. The change of the ratio $N_{irradiated}/N_{as\text{-}prepared}$ from above unity to below unity at about 0.4 ns demonstrates that after electron irradiation both short τ_0 and long lifetime τ_1 and τ_2 components (specimen WC-SNT1, see Table I) dissapear and an intermediate component τ_1 (specimen WC-SNT1, see Table II) appears.

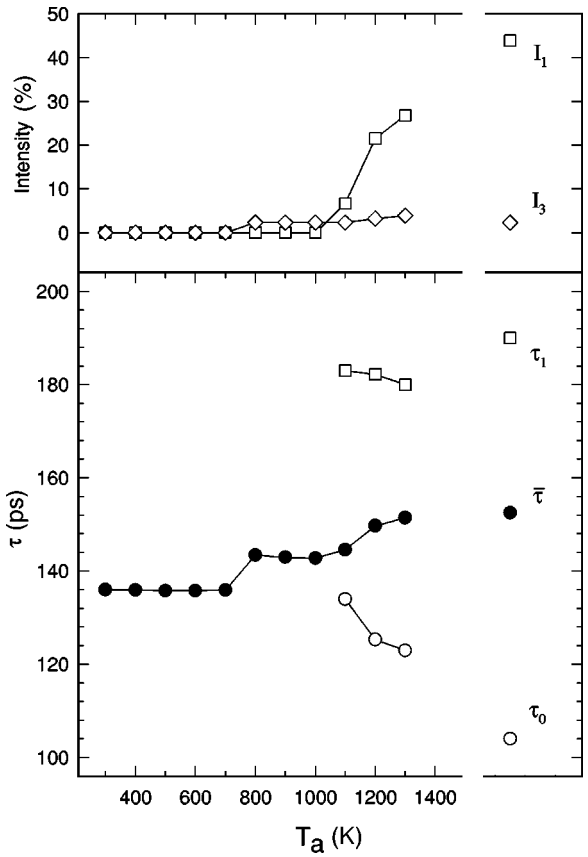

FIG. 2. Intensities I_1 (□) and I_3 (◇) and positron lifetime components τ_0 (○), τ_1 (□) and mean positron lifetime $\bar{\tau}$ (●) in electron irradiated WC ($E_1=1.0$ MeV, $\Phi_1=1.8\times10^{23}$ m^{-2}) versus annealing temperature T_a. On the right-hand side the component intensities and the positron lifetimes for as-prepared WC-HM are depicted (specimen WC-HM, see Table II). The experimental uncertainties are described by the sizes of the symbols.

irradiation of WC have to be considered. For this consideration the threshold energies $E_{d,C}=28$ eV for the displacement of C atoms and $E_{d,W}=42$ eV for the displacement of W atoms determined by electrical resistivity measurement on TaC_y[21] may be used because of the similar physical properties of TaC and WC and the similar atomic masses of the metallic components. In the case of 1-MeV electrons the maximum energy transferred to a W atom[22] $E_{T,W}^{max}=23$ eV is well below $E_{d,W}$ so that no vacancies on the W sublattice but on the C sublattice only are be generated.

The concentrations $c_V=\sigma_d\Phi$ of irradiation-induced vacancies at $T=0$ K are calculated from the total electron doses and the displacement cross sections σ_d which depend on the threshold energies E_d (Ref. 21) (see Table III). The calculation shows that the irradiation with a high dose of 1 MeV electrons gives rise to a high concentration of carbon vacancies well above the limit of saturation of positrons (Table III) and, therefore, well above the concentration of metallic vacancies prior to irradiation. Hence the single positron lifetime component $\tau_1=136\pm3$ ps observed in this state has to be attributed to positron trapping and annihilation in carbon vacancies V_C.

Therefore the positron lifetime $\tau_1=136$ ps in carbon vacancies in WC appears to be significantly lower than that in tungsten vacancies ($\tau_1\simeq160$ ps) in qualitative agreement with the theoretical predictions.[11] The theoretically deduced difference of the positron lifetimes in the two types of vacancies is even higher which might be due to the simplified lattice structure used in the calculations.[11] The enhanced positron lifetime in V_W compared to V_C can be attributed to the lower electron density at the nearest-neighbor sites of the tungsten vacancy which are occupied by carbon atoms exclusively whereas the carbon vacancy is surrounded by tung-

TABLE III. Calculation of irradiation-induced vacancy concentrations c_V for the W and C sublattices in tungsten carbide. E_T^{max}: maximum transferred energy; E_d: threshold energy for atomic displacement; σ_d: displacement cross section.

Sublattice in which vacancies are produced	Energy of incident electrons [MeV]	Dose of incident electrons [m^{-2}]	E_T^{max} [eV]	E_d [eV]	σ_d [barn]	c_V [ppm]
W	1.0 ± 0.1	$(1.8\pm0.2)\times10^{23}$	23 ± 2	(42)[a]	0	0
C	1.0 ± 0.1	$(1.8\pm0.2)\times10^{23}$	370 ± 40	(28)[a]	(25)[a]	450 ± 100
W	2.5 ± 0.2	$(1.2\pm0.1)\times10^{22}$	100 ± 10	(42)[a]	(83)[a]	100 ± 30
C	2.5 ± 0.2	$(1.2\pm0.1)\times10^{22}$	1600 ± 100	(28)[a]	(25)[a]	30 ± 10

[a]Reference 21.

sten atoms with a higher electron density.

In this context one also should point out that the positron lifetime in the carbon vacancies of WC is about 20 ps shorter than the value measured in carbon vacancies in tantalum carbide $TaC_{0.99}$ (Refs. 12 and 17) (Table III). On the one hand, this arises from the different sizes of the carbon vacancy in these compounds. The volume of 0.01 nm^3 of the vacant triangular prism formed by six metal atoms in WC is by a factor of 1.4 smaller than the volume of the vacant octahedron in cubic $TaC_{0.99}$ (lattice parameter $a_{B1}=0.4456$ nm) which is also formed by six atoms. The electron density in the carbon vacancy of WC is further enhanced in comparison to TaC due to one additional valence electron of the W atom.

Considering the irradiation experiment with 2.5 MeV electrons, vacancies V_C and V_W on both sublattices are generated as shown in Table III. Although in this case the carbon vacancy concentration is lower than the total concentration of as-prepared and irradiation-induced metal vacancies, the component $\tau_1=137$ ps characteristic of carbon vacancies occurs. This indicates that competitive positron trapping in metal vacancies is small and therefore that the specific trapping rate of metal vacancies is considerably lower than that of carbon vacancies. The fact that the long-lived component τ_2 still occurs after high-energy irradiation in contrast to the case of low-energy irradiation may arise from the reduced trapping rate of vacancies in the former case due to the lower electron dose.

During isochronal annealing up to 1400 K the defects induced by low-energy irradiation (1 MeV) anneal out in two stages at 800 K and at 1200 K as indicated by the increase in $\overline{\tau}$ of 16 ps to the value of the unirradiated state (Fig. 2). In the 800 K stage the long positron lifetime component τ_2 reappears indicating that the vacancy concentration decreases below the threshold of saturation trapping of positrons. Therefore the 800 K stage is attributed to the annealing out of carbon vacancies presumably by long-range migration. This interpretation is supported by the observation of an order-disorder transition on the C sublattices of NbC_y and TaC_y (Refs. 5 and 23) in the same temperature regime which requires a substantial vacancy mobility. Radiation induced carbon and metal interstitials are supposed to migrate at much lower temperatures at 80 and 175 K, respectively, as concluded from annealing studies of the electrical resistivity of TaC_y after electron irradiation.[24]

The migration of carbon vacancies above 800 K may give rise to the formation of small carbon clusters. These clusters could be dissolved during further annealing in the 1200 K stage. After complete annealing out of the carbon vacancies a positron lifetime spectrum similar as in the as-prepared state occurs with partial positron annihilation in the free state (component τ_0), in W vacancies (component τ_1), and in vacancy agglomerates (component τ_2, see Fig. 2). In conclusion, the present positron lifetime studies of WC after irradiation with electrons of various energies have led to the identifiation of the carbon and metal vacancies with characteristic positron lifetimes.

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*Permanent address: Institute of Solid State Chemistry, Russian Academy of Sciences, Pervomaiskaya 91, GSP-145 Ekaterinburg 620219, Russia.

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