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On the preparation of clean tungsten single crystals

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ABSTRACT

The cleaning procedure consists of two-step-flashing: (i) cycles of low power flashes ($T \sim 1200$ K) at an oxygen partial pressure of $P_{O_2} = 6 \times 10^{-8}$ mbar, to remove the carbon from the surface, and (ii) a single high power flash ($T \sim 2200$ K), to remove the oxide layer. The removal of carbon from the surface through the chemical reaction with oxygen during low power flash cycles is monitored by thermal desorption spectroscopy. The exposure to O_2 leads to the oxidation of the W surface. Using a high power flash, the volatile W-oxides and the atomic oxygen are desorbed, leaving a clean crystal surface at the end of procedure. The method may also be used for cleaning other refractory metals like Mo, Re and Ir.

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Preparing a clean substrate is the first important step toward epitaxial thin film growth. In some cases even a low level of the substrate contamination totally changes the physical properties of the film. Tungsten is a substrate which has attracted much attention by researchers who work on the fundamental physics of thin films and nanostructures [1–23]. The high melting point and absence of intermixing with the overlayer, allowing growth at high temperatures, make it a prime candidate. Moreover, tungsten has a large spin-orbit coupling, which can be used to modify the electronic properties of the overlayer.

Carbon and oxygen are the most familiar contaminants on the tungsten surface. The level of contamination may be below the sensitivity limit of conventional characterization tools like Auger electron spectroscopy (AES). Checking the cleanliness of the substrate by AES or other electron spectroscopy/diffraction tools leads to a surface contamination caused by the e-gun's filament and electron stimulated desorption from the electrodes.

Although several recipes have been proposed for cleaning the W substrates [23–38], the efficiency and details of the procedures are rarely discussed and the cleanliness of the substrate has been an open question. Recently, a scanning tunneling microscopy investigation showed that the level of surface contamination strongly depends on the preparation conditions [39].

In this Letter, we describe a highly efficient cleaning procedure for W single crystals, which has already been developed in our lab more than one and half decades ago. It can be simply applied in all conventional ultra-high vacuum (UHV) systems and be used for cleaning of other refractory metals. An advantage of the method is that the procedure can be monitored *in situ* by a quadrupole mass spectrometer, without the need of an electron beam based spectroscopy.

It is usually observed that the annealing of a W crystal leads to the segregation of carbon from the bulk onto the surface [29,40–43]. The segregation in some cases is so strong that it can be seen in low-energy electron diffraction (LEED) patterns or AES spectra [40,42,43]. Therefore, it has been proposed to anneal the substrate in an oxygen atmosphere. The segregated carbon shall react with oxygen and form CO [44–46]. It can be seen with most surface science methods, e.g. LEED and AES, that the carbon layer can be removed by dosing with O_2 at elevated temperatures ($\geqslant 1200$ K), which forms volatile CO. Annealing for long time causes a lot of heat dissipation into the UHV parts and leads to a bad vacuum. Moreover, a layer of tungsten oxides will form on the surface [31,47–52]. The tungsten oxides and the atomic oxygen can only be removed at very high temperatures up to 2200 K.

In our procedure we use electron bombardment to heat the substrate. A schematic representation of our set-up is given in Fig. 1. In this method a constant positive high voltage is applied to the target. A dc current running through the filament causes an emission current flowing from the filament to the target. The emission current strongly depends on the distance between filament and target and can be adjusted by changing the filament current. In order to avoid the heat dissipation into the UHV parts we used short time heating (flashing).

Our cleaning procedure consists of two steps:

Step (1): Cycles of low power flashes (LPF) in oxygen atmosphere in which the heating power is alternately switched on for 15 s and off for 60 s. This time is essential to have enough oxygen on the surface of the crystal to react with the segregated carbon (an oxygen partial pressure of 5×10^{-8} mbar results in an exposure of about 2.2 L). An emission current of about $I_{emis} =$ 40 mA and a voltage of $V = 1.1$ kV (power: $P = 44$ watts) leads to

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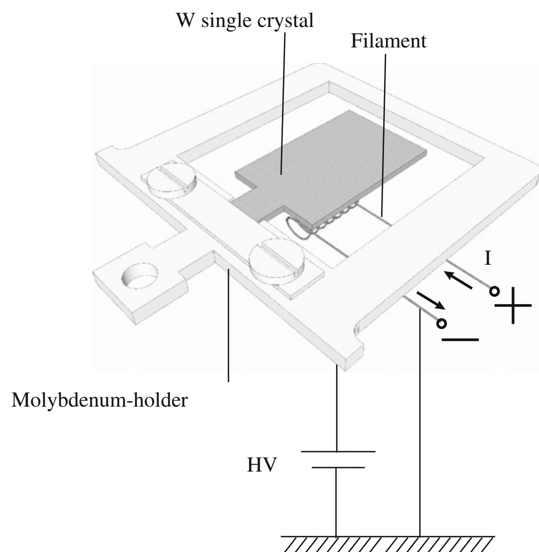

Fig. 1. Schematic illustration of the sample holder and flashing geometry.

a sample temperature of about 1200 K, measured by a pyrometer. This step is used to remove the carbon from the surface through the reaction with the oxygen adsorbed on the surface. The number of cycles depends on the cleanness of the substrate. This step can be monitored by thermal desorption spectroscopy (TDS). For that, the partial pressure of CO and O_2 inside the chamber, measured by a quadrupole mass spectrometer, is monitored as a function of time. Fig. 2 shows typical TD-spectra recorded during the cleaning of a W(1 1 0) single crystal, in which both CO (mass = 28) and O_2 (mass = 32) partial pressures are recorded as a function of time. As the heating power is switched on, a dip in oxygen and a peak in CO partial pressures are observed. The dip in the oxygen partial pressure is attributed to the reaction of oxygen with carbon and formation of CO. The formed CO causes a peak in the partial pressure of CO. The slow increase of the O_2 partial pressure after each heating cycle is due to the uptake of oxygen with diminishing sticking coefficient of O_2. Saturation is reached faster at higher partial pressures.

Now, we discuss the behavior of TD-spectra of CO in more detail. Fig. 3 shows another series of TD-spectra of CO measured during a set of LPF cycles used to clean a W(1 1 0) crystal. One clearly sees the evolution of the CO desorption peak after each

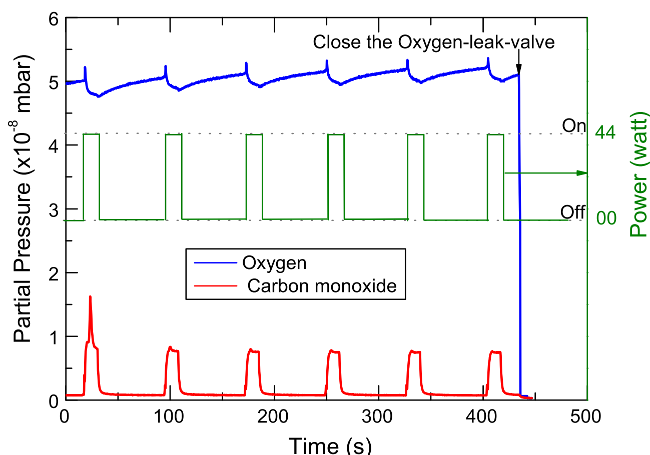

Fig. 2. Thermal desorption spectra during subsequent LPF cycles of W(1 1 0) crystal, at 6×10^{-8} mbar of O_2 exposure. Both CO and O_2 partial pressures are monitored.

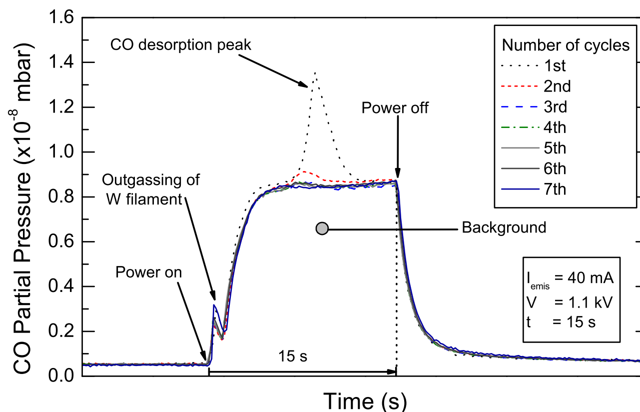

Fig. 3. Thermal desorption spectra during subsequent LPF cycles of W(1 1 0) crystal, at 6×10^{-8} mbar of O_2 exposure.

cycle. In each spectrum first small sharp peak is due to the outgassing of the W filament. This feature is followed by an increase of CO partial pressure due to the heat dissipation onto the sample holder and chamber's atmosphere, giving rise to a flat background in the spectra. In addition, a CO desorption peak arises above the background. As mentioned above, this peak is due to the chemical reaction of C on the crystal surface with the adsorbed oxygen, desorbing CO. The sudden decrease of CO partial pressure in the end of each cycle marks the switch off of the heating filament. Fig. 3 shows the gradual decrease of the CO desorption peak from the crystal during the sequence of flashing cycles, until it completely vanishes. The number of LPFs needed to completely remove C depends on the cleanness of the crystal. For cleaning a substrate that is freshly loaded into UHV the number of cycles is larger than for the one that had been prepared several times.

Step (2): A single high power flash (HPF) at vacuum ($T \sim 2200$ K) to remove the oxide layer. In our construction this temperature can be achieved by an emission current of $I_{emis} = 160$ mA and a voltage of $V = 1.1$ kV (power: $P = 176$ watts). Actually, the tungsten oxide is desorbed at $T \sim 1500$ K, while heating to 2200 K is necessary to remove the atomic oxygen [53,54].

In order to test the efficiency of this procedure, one can perform AES. But the level of contamination might be below the sensitivity limit of AES. Moreover, it leads to a surface contamination caused by the e-gun's filament and electron stimulated desorption from the electrode. We propose to do a HPF in an oxygen atmosphere at the end of the cleaning (as a test run), i.e., subsequent to the last

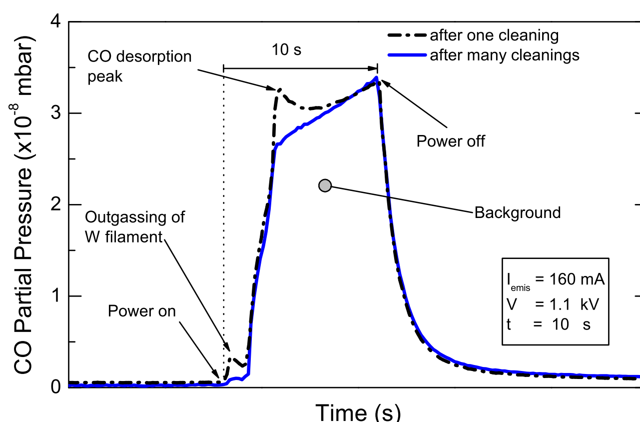

Fig. 4. Two HPFs at 6×10^{-8} mbar of O_2 (test runs), after performing the cleaning procedure once (dash-dotted curve) and many times (solid curve), to check the efficiency of the cleaning procedure.

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HPF in vacuum. If the segregation of carbon during the last HPF is too much, a strong CO peak should be observed in the test run. In Fig. 4, two different test runs are compared: the dash-dotted curve, measured after one cleaning procedure, and the solid curve, obtained after repeating the procedure many times. No CO peak could be observed in the solid curve, evidencing an effective procedure for removing of the carbon contamination from the surface and its depletion in the bulk.

In conclusion, we present a method for cleaning the tungsten single crystals. The method basically consists of two-step-flashing of the crystal. In the first step the carbon contamination is removed via reaction with oxygen admitted into the UHV system. In the second step the oxide layer and atomic oxygen are removed by flashing at high temperature. TDS is used to monitor the procedure in each step and to check the efficiency of the method. The main advantage of our method is that it can simply be applied in all conventional UHV systems, without the use of AES. In cross-checks, we found that C-contamination from the electron gun (deposited during the measurement of the Auger spectra) can be removed as well. This method may also be applied to the other refractory metals like Mo, Re and Ir.

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References

[1] H.J. Elmers, Int. J. Mod. Phys. B 9 (1995) 3115.
[2] M. Pratzer, H.J. Elmers, M. Bode, O. Pietzsch, A. Kubetzka, R. Wiesendanger, Phys. Rev. Lett. 87 (2001) 127201.
[3] M. Pratzer, H.J. Elmers, Phys. Rev. B 67 (2003) 094416.
[4] U. Gradmann, G. Liu, H.J. Elmers, M. Przybylski, Hyperfine Interact. 57 (1990) 1845.
[5] H.J. Elmers, J. Hauschild, U. Gradmann, J. Magn. Magn. Mater. 221 (2000) 219.
[6] M. Przybylski, U. Gradmann, Phys. Rev. Lett. 59 (1987) 1152.
[7] H.J. Elmers, J. Hauschild, U. Gradmann, Phys. Rev. B 54 (1996) 15224.
[8] S. Stankov, R. Röhlsberger, T. Ślęzak, M. Sladecek, B. Sepiol, G. Vogl, A.I. Chumakov, R. Rüffer, N. Spiridis, J. Łażewski, K. Parlinski, J. Korecki, Phys. Rev. Lett. 99 (2007) 185501.
[9] D. Sander, A. Enders, J. Kirschner, IEEE Trans. Magn. 34 (1998) 2015.
[10] D. Sander, R. Skomski, A. Enders, C. Schmidthals, D. Reuter, J. Kirschner, J. Phys. D: Appl. Phys. 31 (1998) 663.
[11] D. Sander, A. Enders, C. Schmidthals, J. Kirschner, H.L. Johnston, C.S. Arnold, D. Venus, J. Appl. Phys. 81 (1997) 4702.
[12] C. Schmidthals, D. Sander, A. Enders, J. Kirschner, Surf. Sci. 417 (1998) 361.
[13] J. Malzbender, M. Przybylski, J. Giergiel, J. Kirschner, Surf. Sci. 414 (1998) 187.
[14] D. Sander, A. Enders, C. Schmidthals, D. Reuter, J. Kirschner, Surf. Sci. 402–404 (1998) 351.
[15] D. Reuter, G. Gerth, J. Kirschner, Phys. Rev. B 57 (1998) 2520.
[16] D. Sander, A. Enders, J. Kirschner, Europhys. Lett. 45 (1999) 208.
[17] D. Sander, A. Enders, J. Kirschner, J. Magn. Magn. Mat. 198–199 (1999) 519.
[18] D. Sander, R. Skomski, C. Schmidthals, A. Enders, J. Kirschner, Phys. Rev. Lett. 77 (1996) 2566.
[19] E. Bauer, H. Poppa, Thin Solid Films 121 (1984) 159.
[20] C. Koziol, G. Lilienkamp, E. Bauer, Phys. Rev. B 41 (1990) 3364.
[21] J. Kolaczkiewicz, E. Bauer, Surf. Sci. 256 (1991) 87.
[22] H. Pinkvos, H. Poppa, E. Bauer, J. Hurst, Ultramicroscopy 47 (1992) 339.
[23] H. Knoppe, E. Bauer, Phys. Rev. B 48 (1993) 5621.
[24] J. Anderson, W.E. Danforth, J. Franklin Inst. 279 (1965) 160.
[25] R.M. Stern, Appl. Phys. Lett. 5 (1964) 218.
[26] A. Elbe, G. Meister, A. Goldmann, Surf. Sci. 371 (1997) 438.
[27] J.W. May, L.H. Germer, J. Chem. Phys. 44 (1966) 2895.
[28] L.N. Tharp, E.J. Scheibner, J. Appl. Phys. 38 (1967) 3320.
[29] D.F. Ollis, M. Boudart, Surf. Sci. 23 (1970) 320.
[30] R. Baudoing, R.M. Stern, Surf. Sci. 10 (1968) 392.
[31] J.C. Buchholz, G.-C. Wang, M.G. Lagally, Surf. Sci. 49 (1975) 508.
[32] J.G. Macmillan, A.J. Slavin, K.J. Sunderland, Surf. Sci. 173 (1986) 138.
[33] U. Gradmann, G. Waller, Surf. Sci. 116 (1986) 539.
[34] F.A. Flitsch, J.R. Swanson, C.M. Friend, Surf. Sci. 245 (1991) 85.
[35] B.G. Johnson, P.J. Berlowitz, D.W. Goodman, C.H. Bartholomew, Surf. Sci. 217 (1989) 13.
[36] J.E. Houston, Surf. Sci. 255 (1991) 303.
[37] A. Fedorus, E. Bauer, Surf. Sci. 418 (1998) 420.
[38] T.O. Mentes, A. Locatelli, L. Aballe, E. Bauer, Phys. Rev. Lett. 101 (2008) 085701.
[39] M. Bode, S. Krause, L. Berbil-Bautista, S. Heinze, R. Wiesendanger, Surf. Sci. 601 (2007) 3308.
[40] H.-W. Fink, G. Ehrlich, Surf. Sci. 110 (1981) L611.
[41] N.R. Gall, E.V. Rutkov, A.Y. Tontegode, Izv. Akad. Nauk Seriya Fiz. 62 (1998) 1980.
[42] K.J. Rawlings, S.D. Foulias, B.J. Hopkins, J. Phys. C: Solid State Phys. 14 (1981) 5411.
[43] J.-M. Chen, C.A. Papageorgopoulos, Surf. Sci. 20 (1970) 195.
[44] L.R. Clavenna, L.D. Schmidt, J. Vac. Sci. Technnol. 9 (1972) 668.
[45] Y. Viswanath, L.D. Schmidt, J. Chem. Phys. 59 (1973) 4184.
[46] J.A. Becker, E.J. Becker, R.G. Brandes, J. Appl. Phys. 32 (1961) 411.
[47] B.J. Hopkins, G.D. Watts, A.R. Jones, Surf. Sci. 52 (1975) 715.
[48] C.W. Tucher, J. Chem. Phys. 47 (1967) 1880.
[49] N.R. Avery, Surf. Sci. 33 (1972) 107.
[50] T. Engle, H. Niehus, E. Bauer, Surf. Sci. 52 (1975) 237.
[51] E. Bauer, T. Engel, Surf. Sci. 71 (1978) 695.
[52] H.M. Kramer, E. Bauer, Surf. Sci. 93 (1980) 407.
[53] Y.G. Ptushinskii, B.A. Chuikov, Surf. Sci. 6 (1967) 42;
Y.G. Ptushinskii, B.A. Chuikov, Surf. Sci. 7 (1967) 90;
Y.G. Ptushinskii, B.A. Chuikov, Fiz. Tverd. Tela 10 (1968) 772.
[54] N.P. Vas'ko, Y.G. Ptushinskii, B.A. Chuikov, Surf. Sci. 14 (1969) 448.