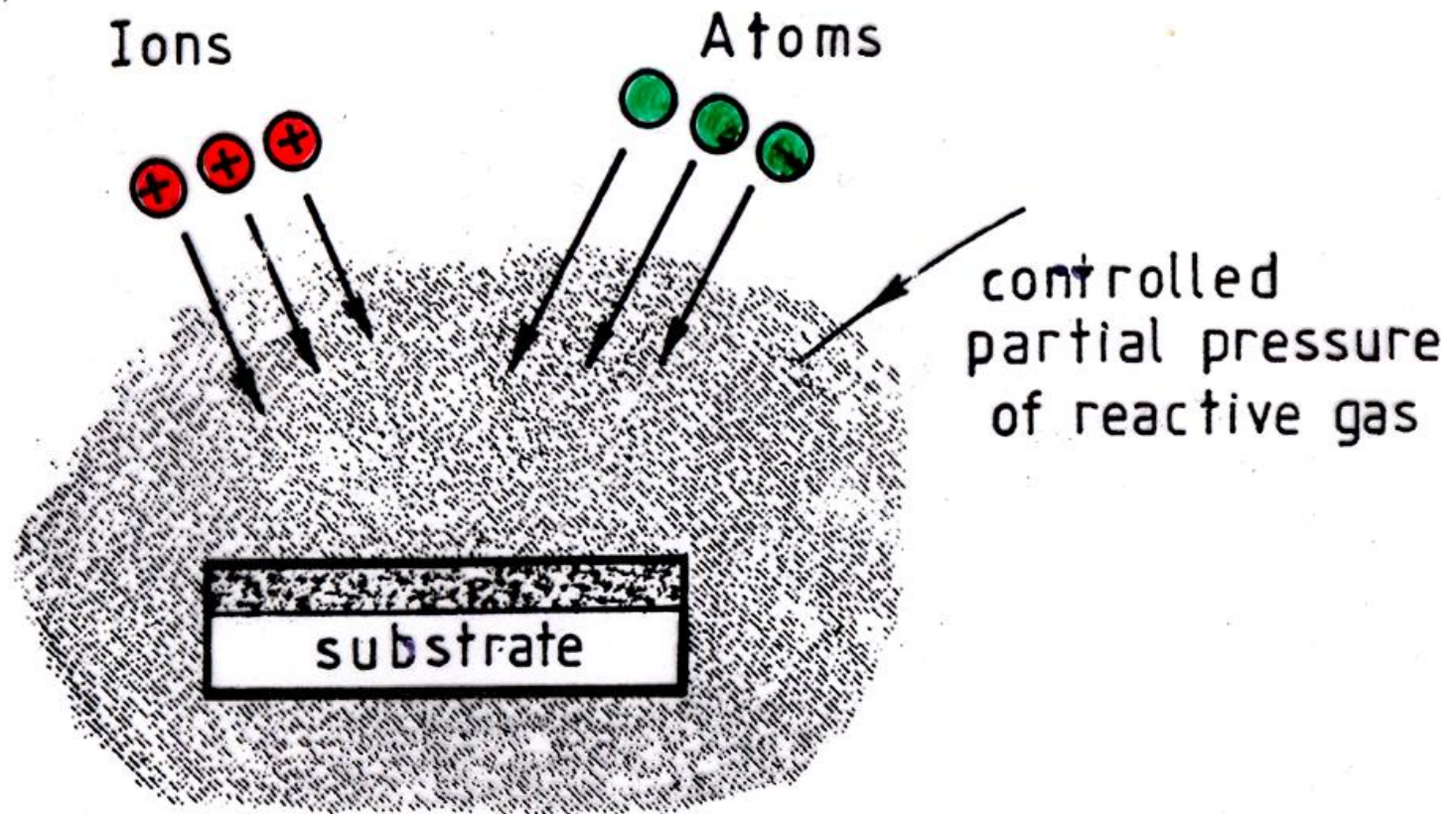


Effects of Energy-Assistance on Coating Microstructure

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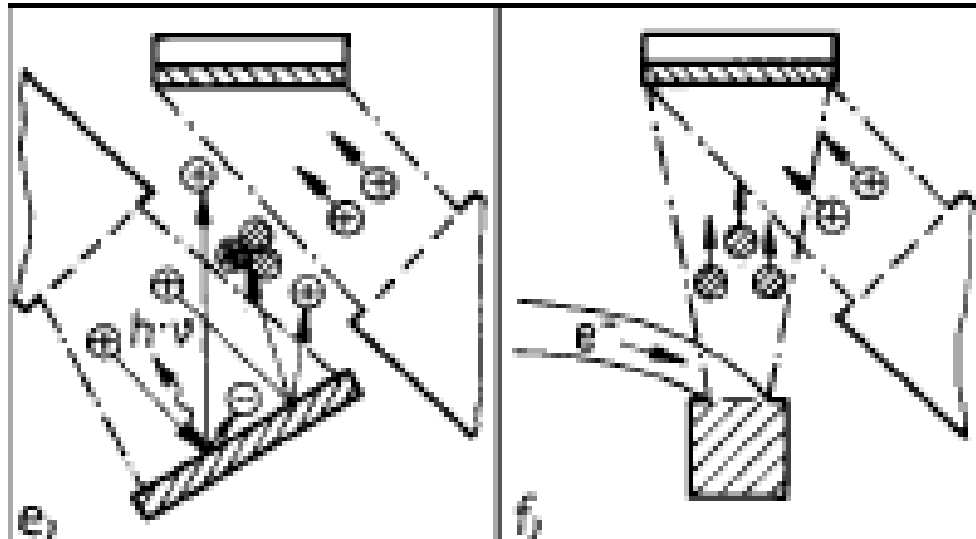
**An Argon ion at 100 eV travels at 70 km/sec
At 10keV it travels at 700km/sec**

**Maximum Energy transfer by a 1000eV Ar ion in a
head-on collision with a Ti atom is 990eV**

**This means some Ti atoms move into the sample
with almost the same energy as the Ar ion had**

**Further collisions cause displaced atoms
(radiation damage) and some energetic atoms
move back to the surface**

**If the outgoing atom transfers energy to a
surface atom greater than the Binding Energy
the atom is sputtered**



Christian Weissmantel: JVST 18 (1981) 179:
Karl-Marx-Stadt

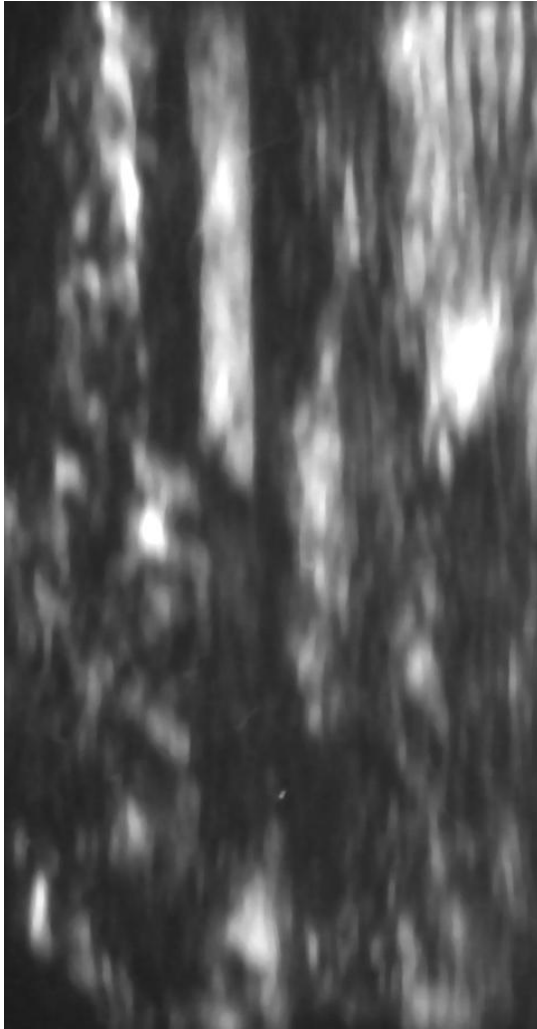


DUAL BEAM ION-ASSISTED DEPOSITION SYSTEM

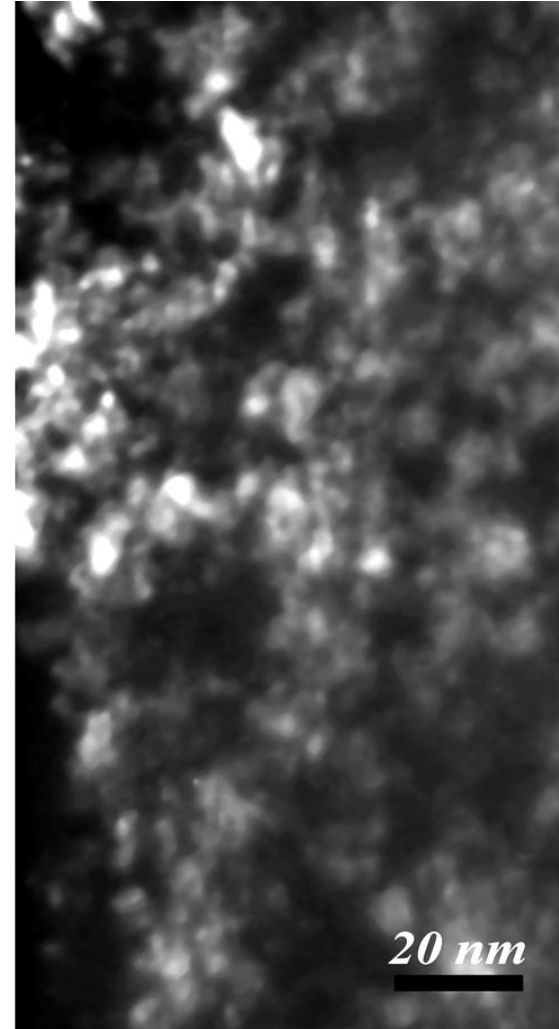


Manchester
Metropolitan
University

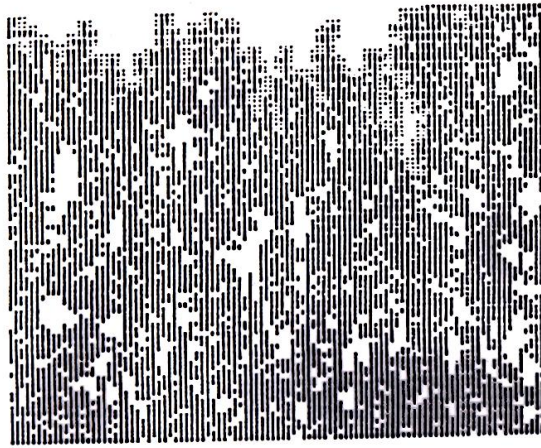
Dark field images of TiN films grown at 473K



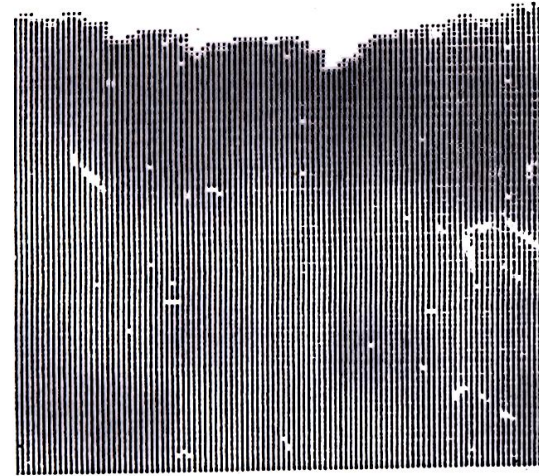
Non-ion assisted



**200 eV N ion assist.
ion/atom ratio 0.5**



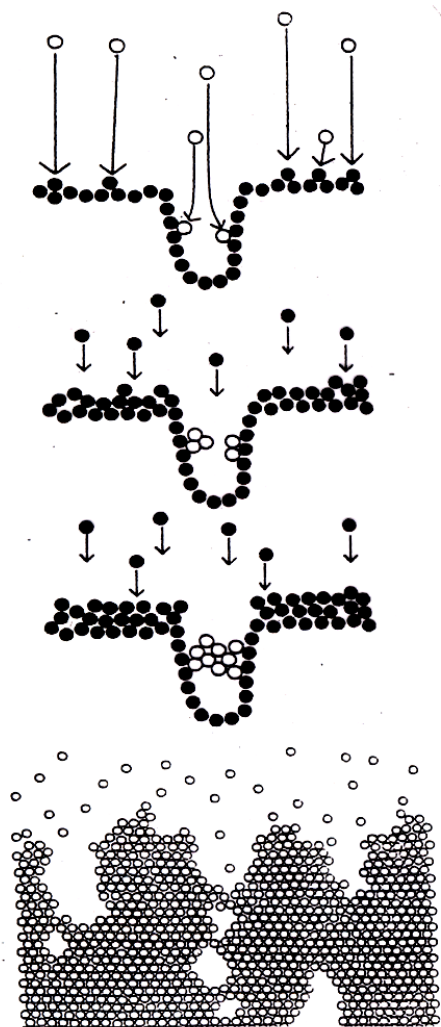
No ion-assist



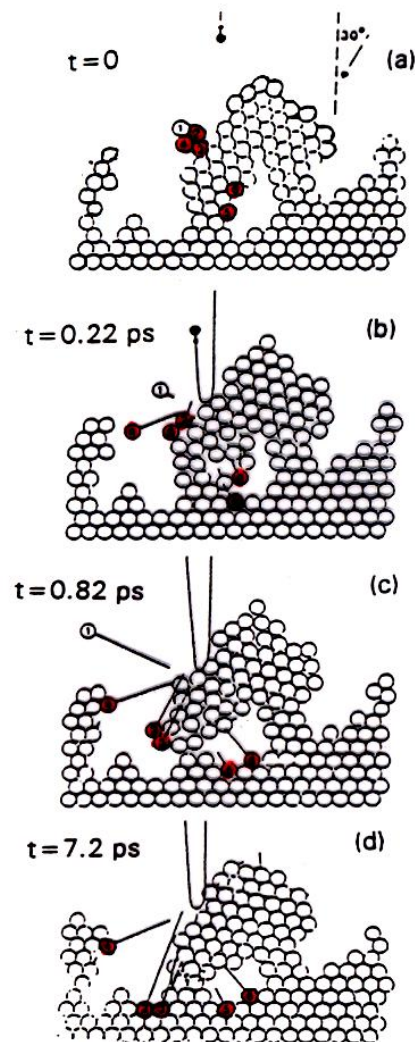
Ion-assist

Effect of 50 eV Ar ion assist on microstructure of Si for
Ar/Si ratio of 0.5

J.Ferron, R.R.Koropecke and R.Arce
Phys.Rev. B35 7611 (1986)



Model by R W Smith and D J
Srolowitz J.Appl Phys. 79 (1996) 1448.
NO ION-assist



MD Simulation for 100eV Ar-Ni IAD
K-H Muller Phys Rev B 35(1987)
7906

IS THE RULE THEREFORE 10-100eV PER ATOM WITH PREFERENCE FOR LOW ENERGY IONS?

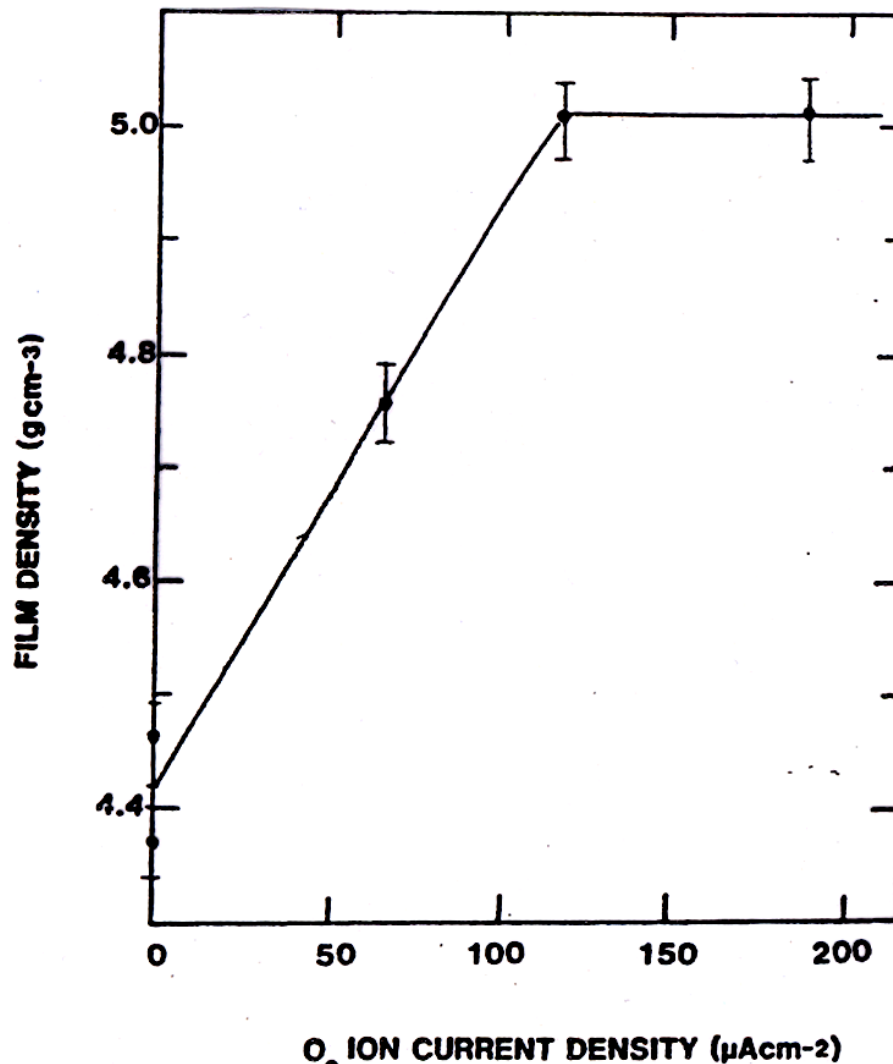
YES IN PRINCIPLE BUT THERE ARE FURTHER CONDITIONS

1. YOU REALLY NEED THE SAME NUMBER OF IONS AND COATING ATOMS ARRIVING AT THE SURFACE PER UNIT TIME (Otherwise some atoms in the coating are buried before they experience the added energy pulse)

e.g. If depositing a monolayer of coating per second (about 6×10^{14} atoms/cm²) you need the same ion bombardment density.

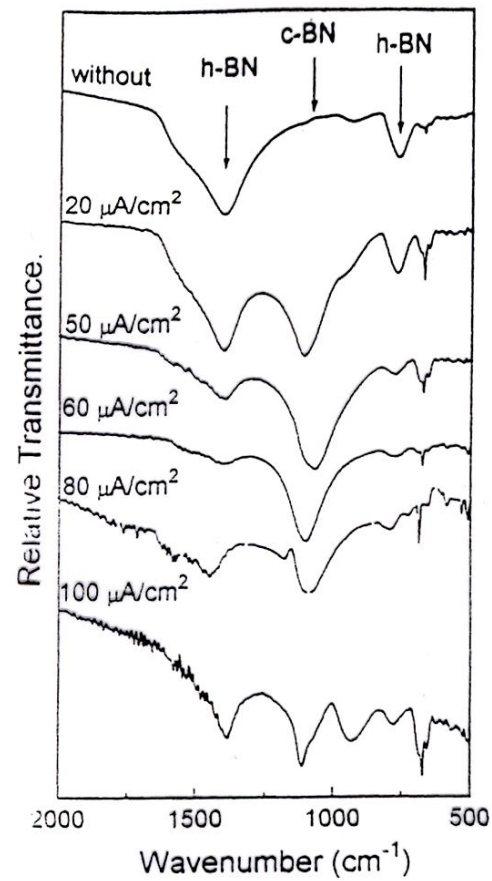
1 microamp-sec is 1×10^{-6} Coulomb. Each ion brings 1.6×10^{-19} Coulomb so at 1 microamp you bring approx 6×10^{12} ions to the surface.

You need 100 times this rate (100 microamp/sec) to match the arrival rate of coating particles. Many systems do not use this current density which means coating atoms are buried before they can experience added energy. Clearly, the conditions are better using the HIPIMS sputtering mode where many coating particles are ionised.



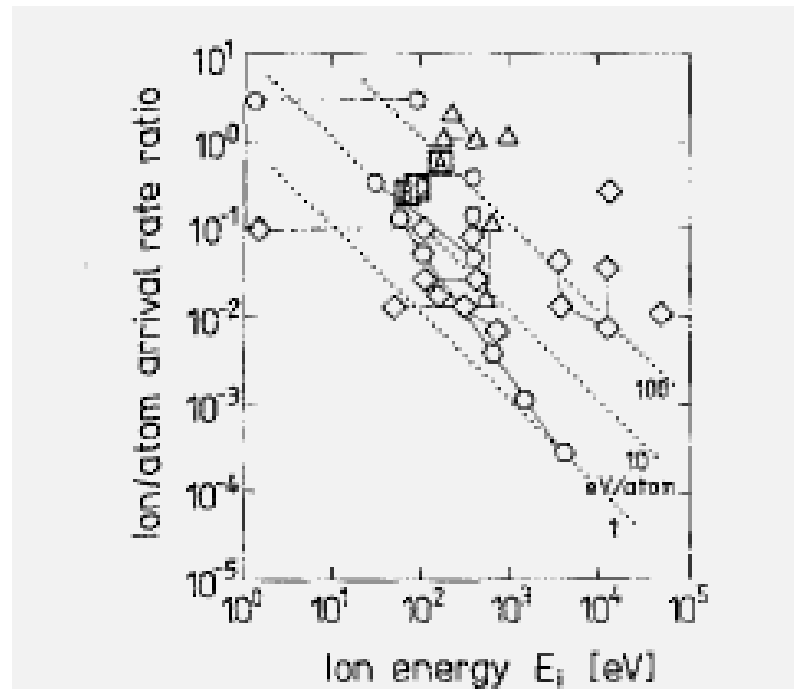
Density change with O_2 Ion Current Density ($\mu A cm^{-2}$)
Density change with Oxygen ion-assistance of evaporated ZrO_2
(Note that for full film density you need $120 \mu A/cm^2$)

P.J.Martin, H.A.MacLeod, R.P.Netterfield and W.G.Sainty
Applied Optics 22, 178 (1983)



**50/50 400eV Ar/N ions on 400 deg C
substrate**

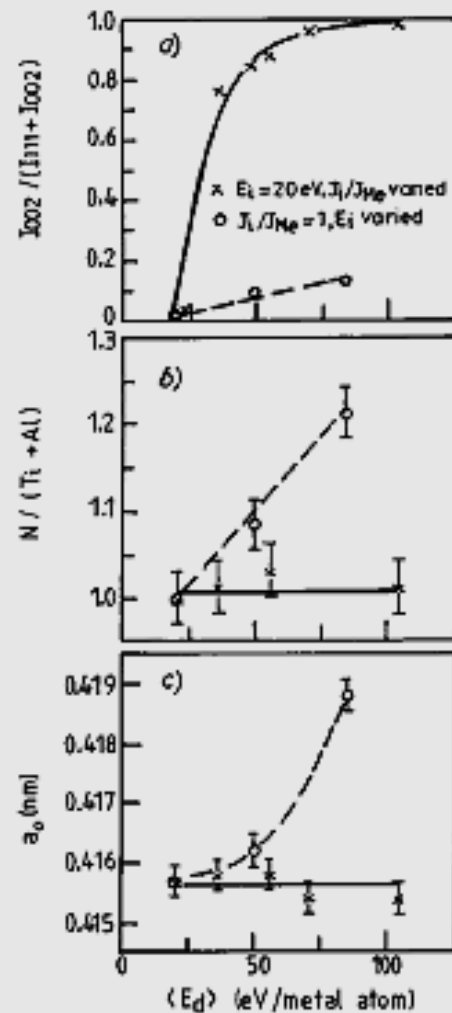
Park et al JVST A15 (1997) 1041



Relation between ion-assist energy and ion/atom ratio required to make significant changes in coating properties.

A: SiN_x, B: SiO₂, C : αC:H. Martinu et al , JVST A12 (1994) 1360- 1364

[Other data from Harper et al o-siO₂, Δ- other dielectrics, ◇-metals, ◊-semiconductors in “Ion Bombardment Modification of Surfaces” ed O.Auciello and R.Kelly. Elsevier , Amsterdam, 1984]



Note: you can achieve the same added energy per atom by using five 20eV ions/atom or one 100eV ion/atom but coating properties are quite different

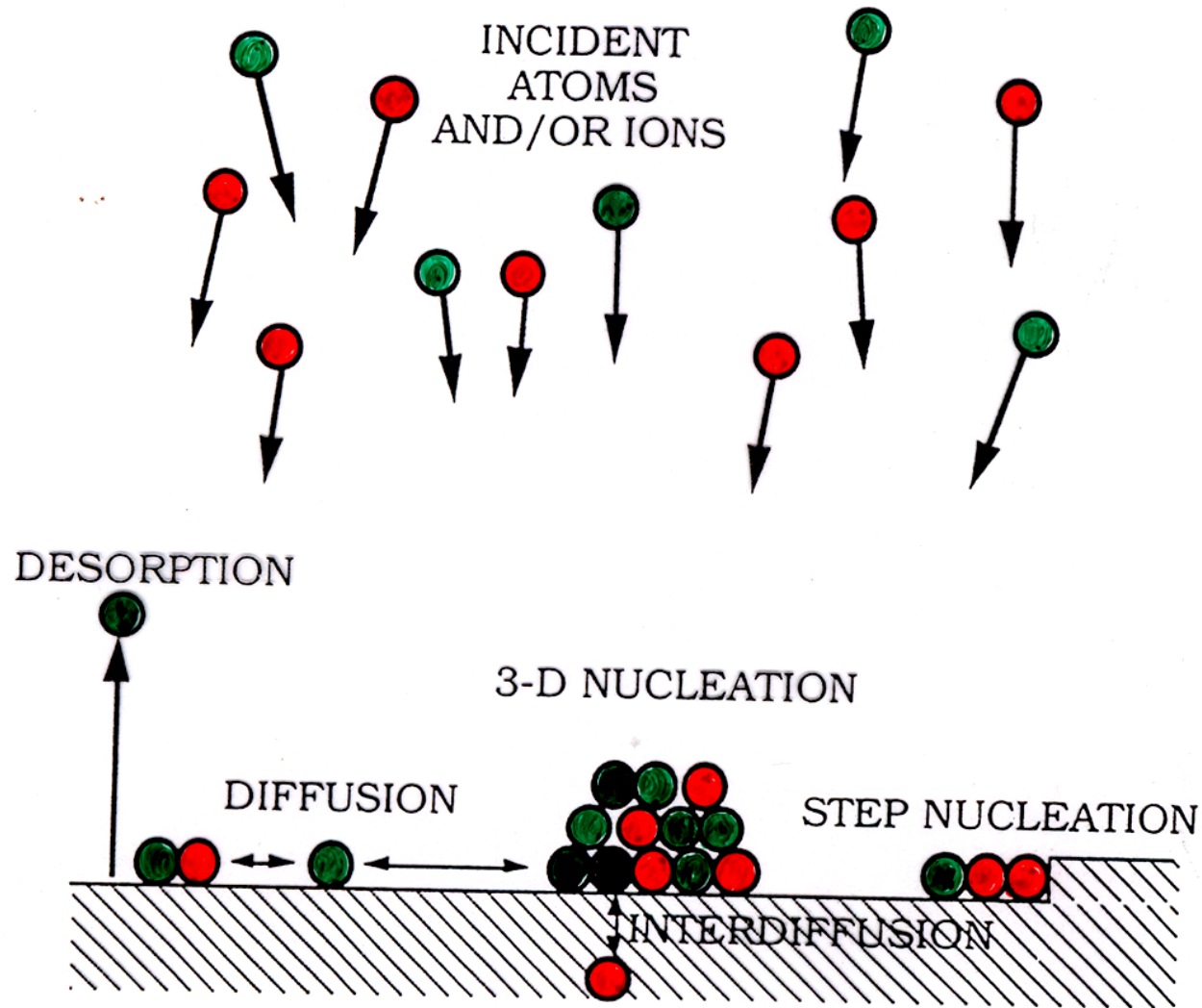
Petrov et al $Ti_{0.5}Al_{0.5}N$ Phys Lett 63 (1993) p36

IS THE RULE THEREFORE 10-100eV PER ATOM WITH PREFERENCE FOR LOW ENERGY IONS and AT LEAST 1 ION PER DEPOSITING ATOM?

YES IN PRINCIPLE BUT THERE IS A FURTHER CONDITION

2. IMPURITIES CAN MODERATE THE FILM NUCLEATION AND GROWTH

Remember that, at 10^{-6} mbar and sticking coefficient of gas 1.0, a perfectly clean surface is completely covered with gas in 0.6 seconds

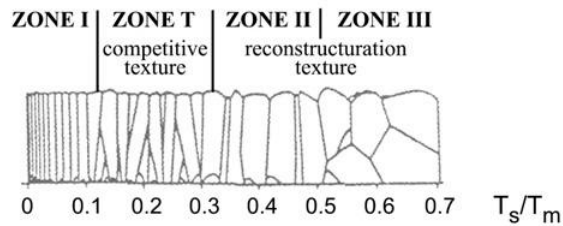


Impurity atoms on the surface (or even atoms of a second component of the coating) can block the diffusion and alter growth morphology

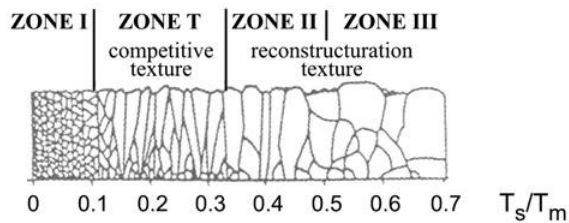
Barna and Adamik's SZM
Effect of impurities or additives

content

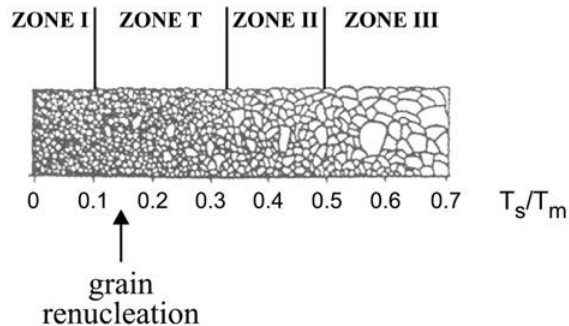
low



medium



high

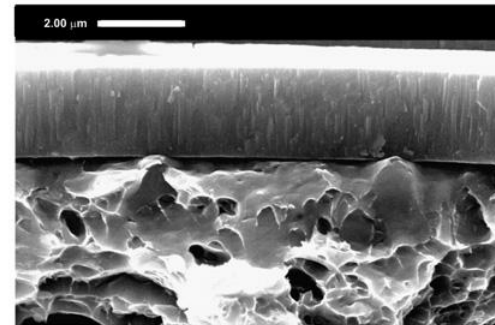


P.B. Barna, M. Adamik, in: Y. Pauleau, P.B. Barna (Eds.),
Protective Coatings and Thin Films,
Kluwer Academic Publishers, the
Netherlands, 1997, p. 279.

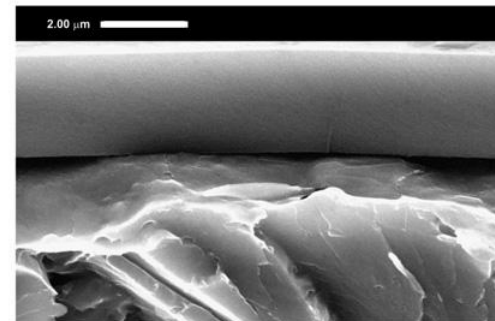
Zr-Cu-N nanocomposite

$$T_s/T_m = 0.18$$

1.2 at.% Cu

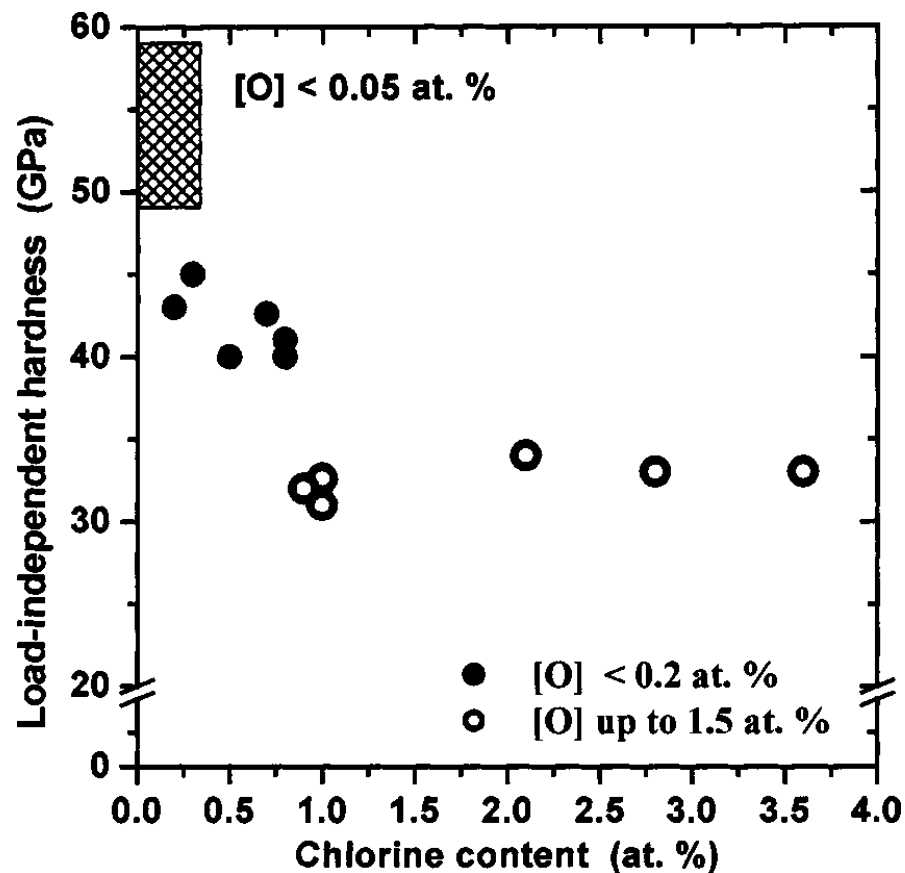
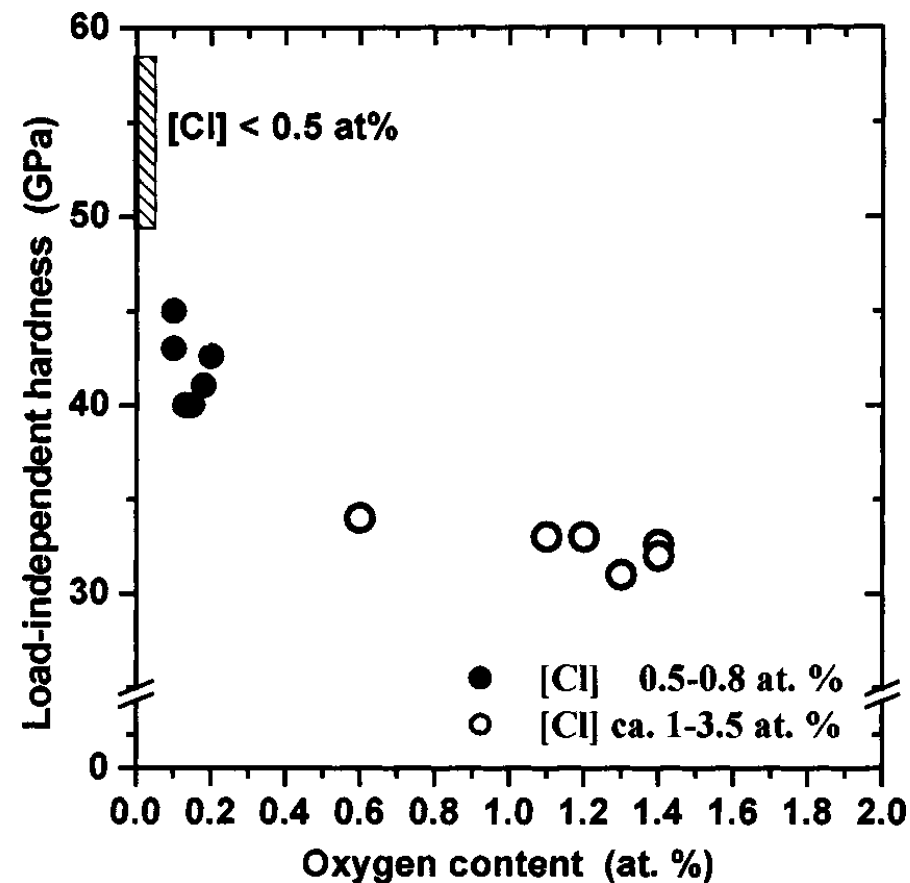


20 at.% Cu

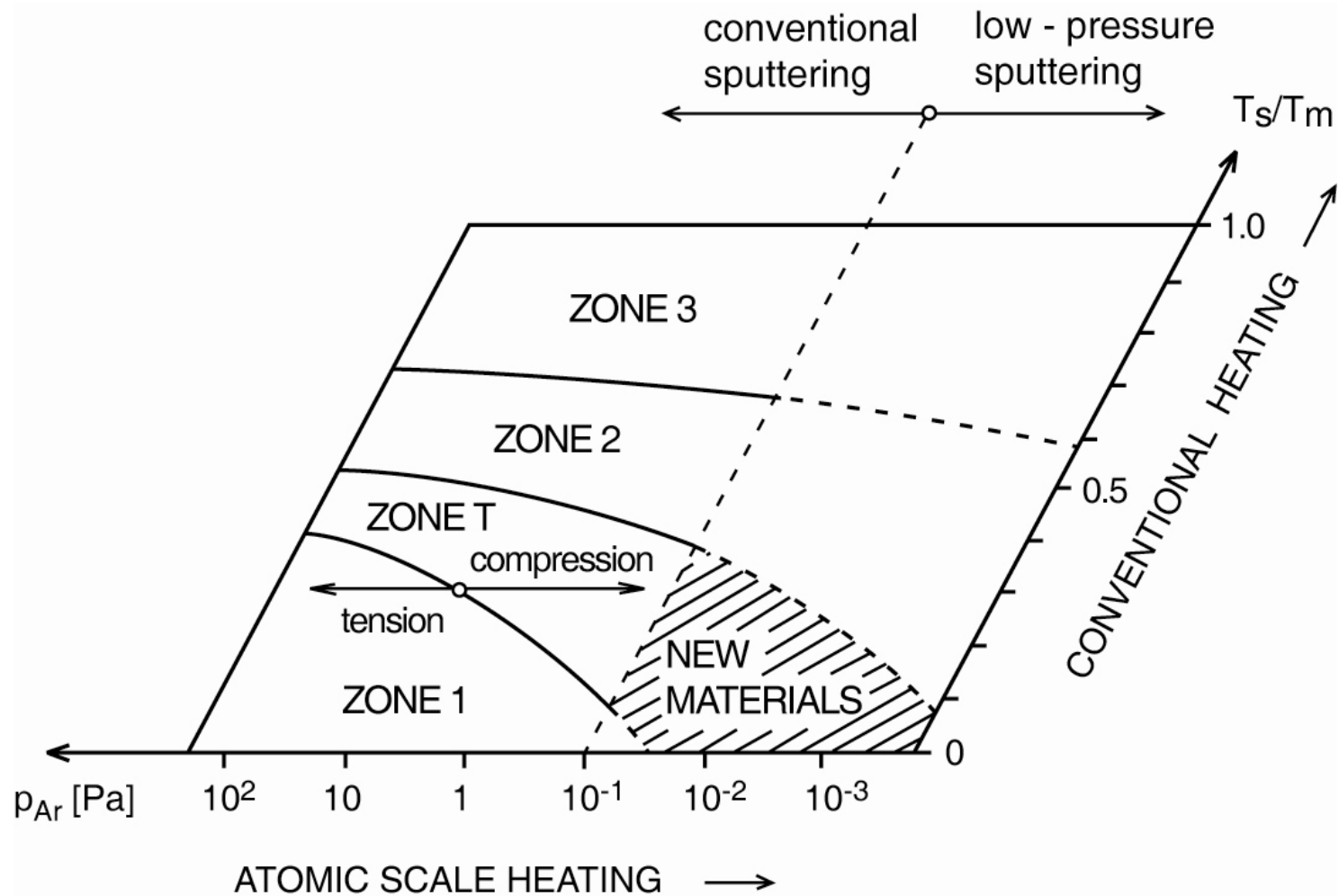


J. Musil, J. Vlček, Surf. Coat.
Technol. 142–144 (2001) 557.

Example showing effect of Cu on
Zr-N morphology

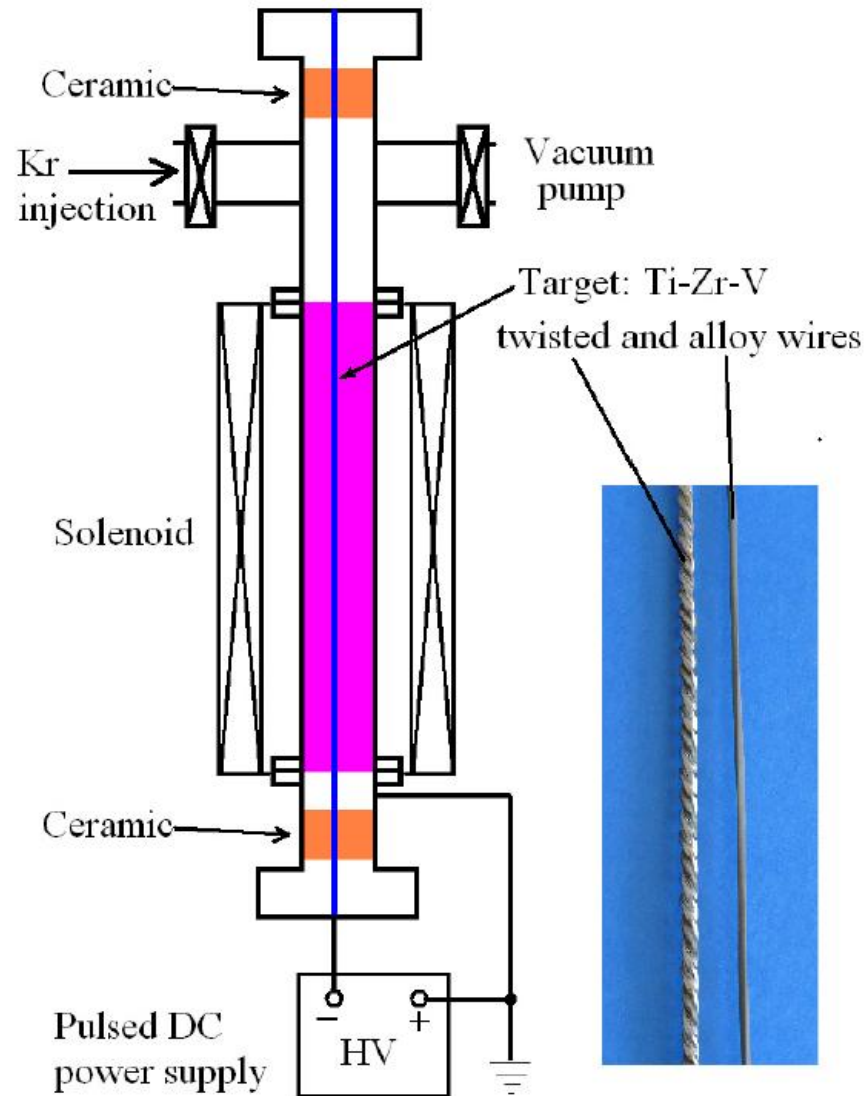


Effect of low levels of impurity on microhardness of nc TiN/a-Si₃N₄
 S. Veprek, H.-D. Maennling, A. Niederhofer, D. Ma and S. Mukherjee
 JVST B 22(5) (2004) L5-L9



Hard nanocomposite coatings: Thermal stability, oxidation resistance and toughness

J. Musil SCT 207 (2012) 50 - 65

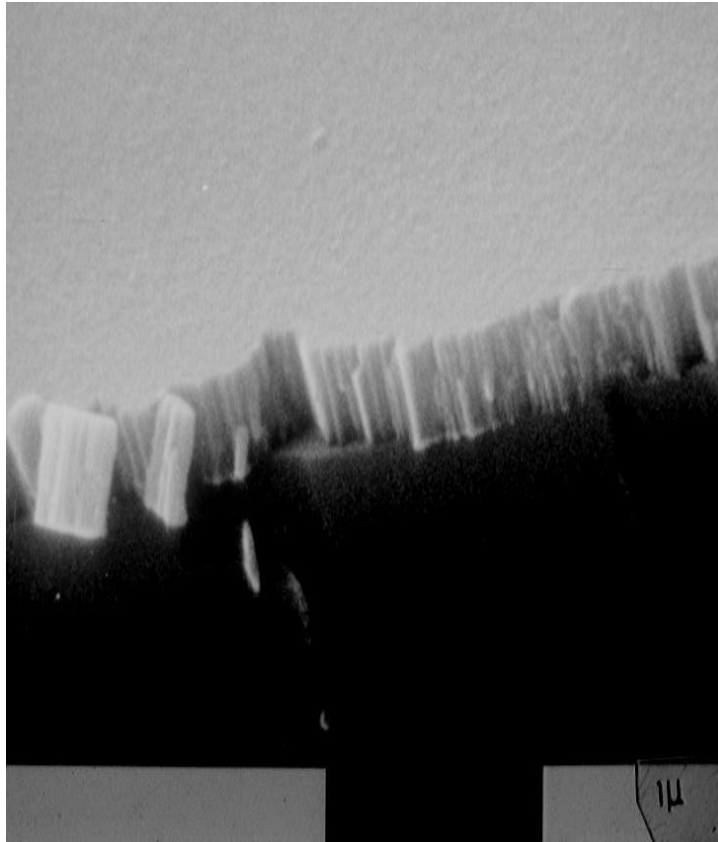


INTERNAL COATING OF TiZrV FILMS ON TUBES

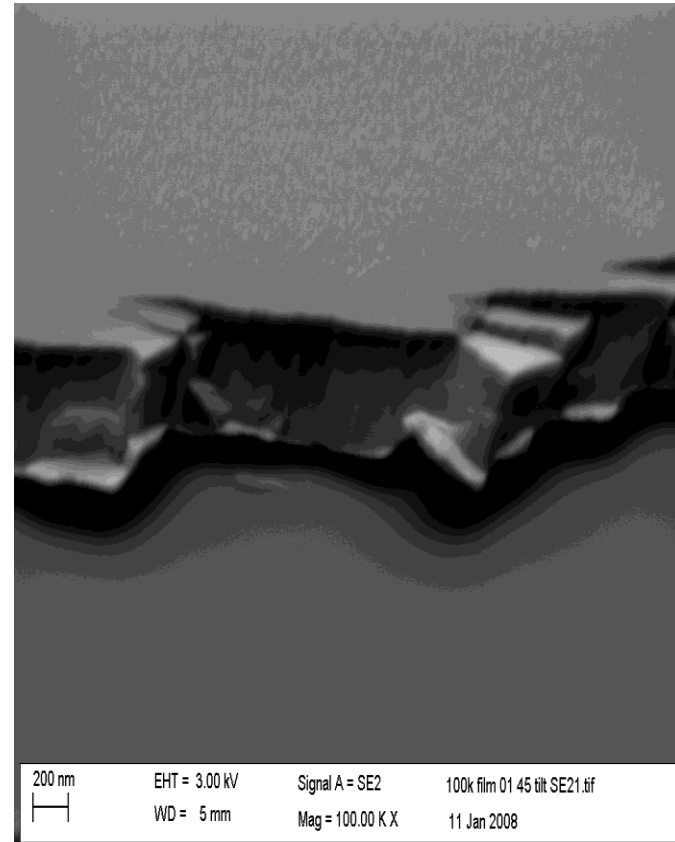
R.Valizadeh, O.B.Malyshev, J.S.Colligon et al.

JVST A27 (3) (2010) 521 - 530

(a) 10^{-2} mbar



(b) 2×10^{-3} mbar with DC pulsed power supply



Science & Technology
Facilities Council

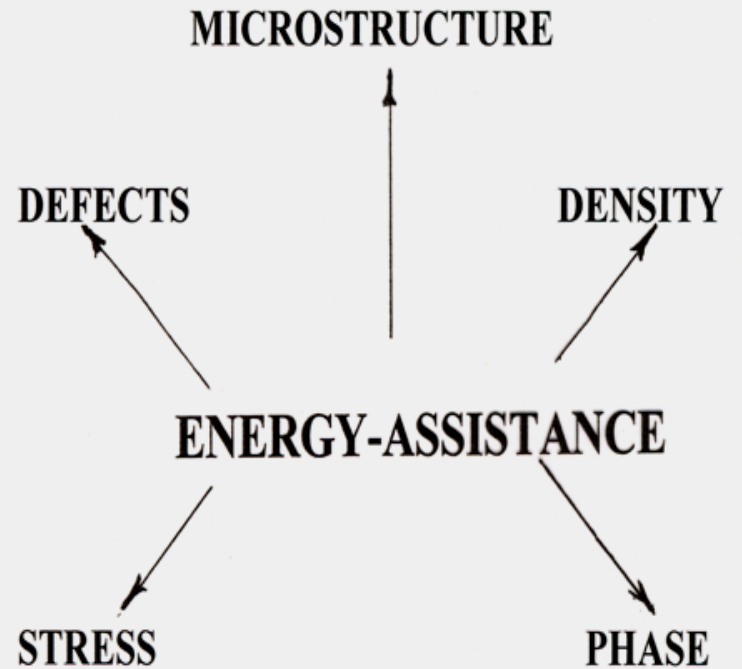
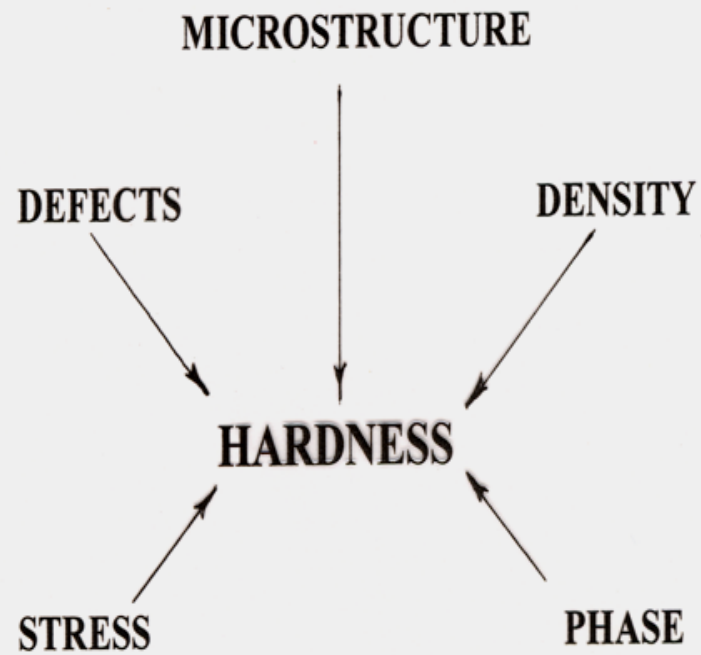


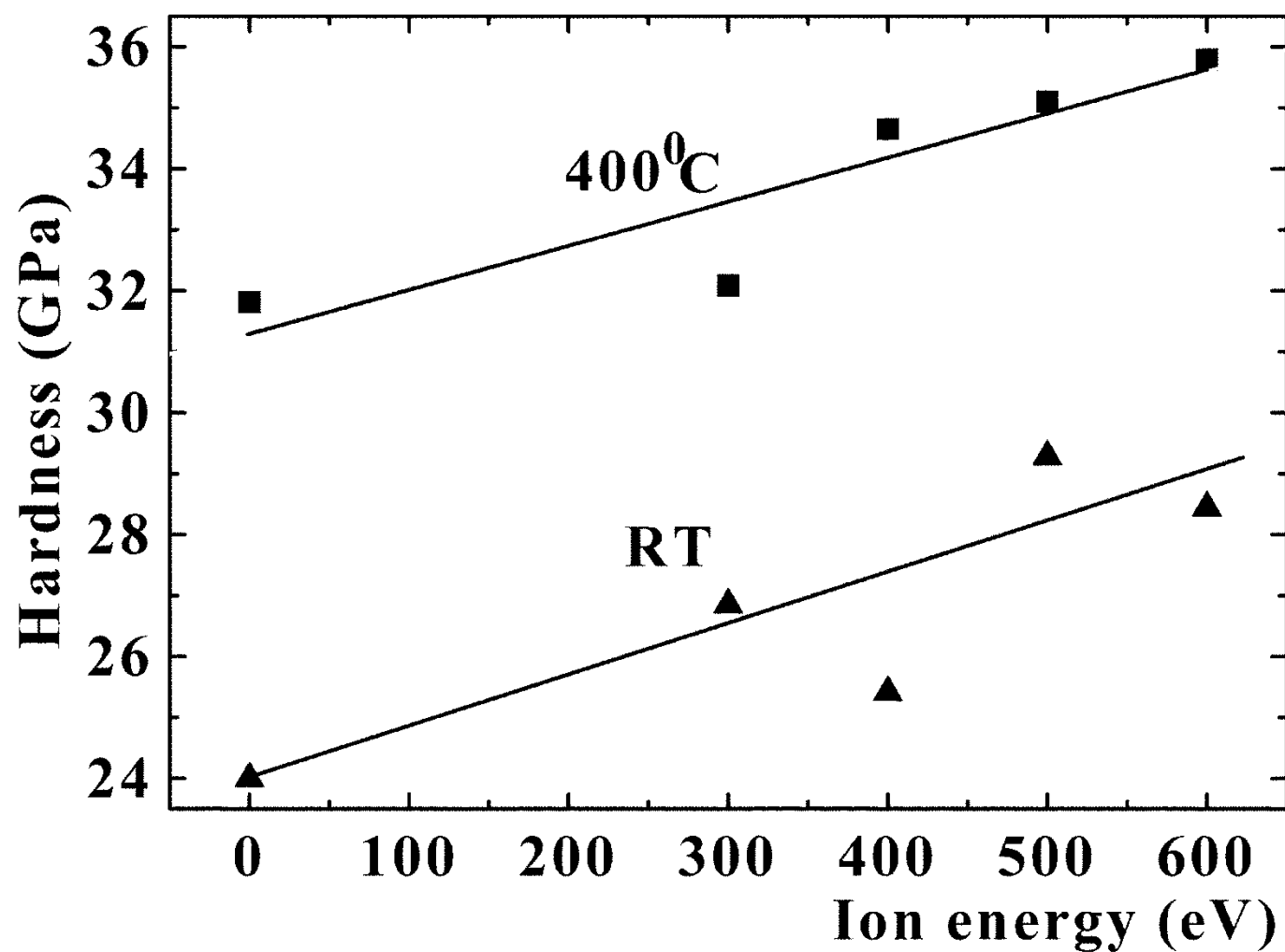
NON-EVAPORABLE TiVZr COATING WITH DIFFERENT MICROSTRUCTURE

**R.Valizadeh, O.B.Malyshev, J.S.Colligon et al.
JVST A 27 (3)(2009) 521 -530**



Manchester
Metropolitan
University

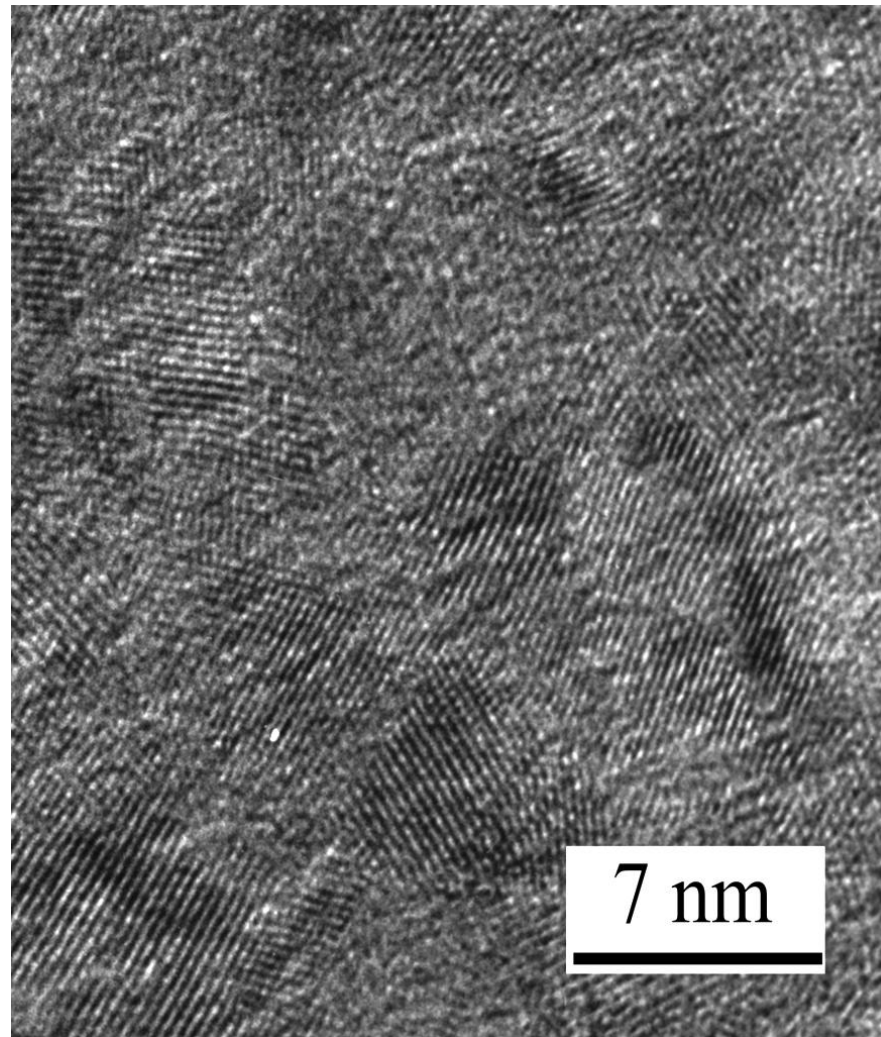




Effect of IAD and T on hardness of Ti-Si-N films

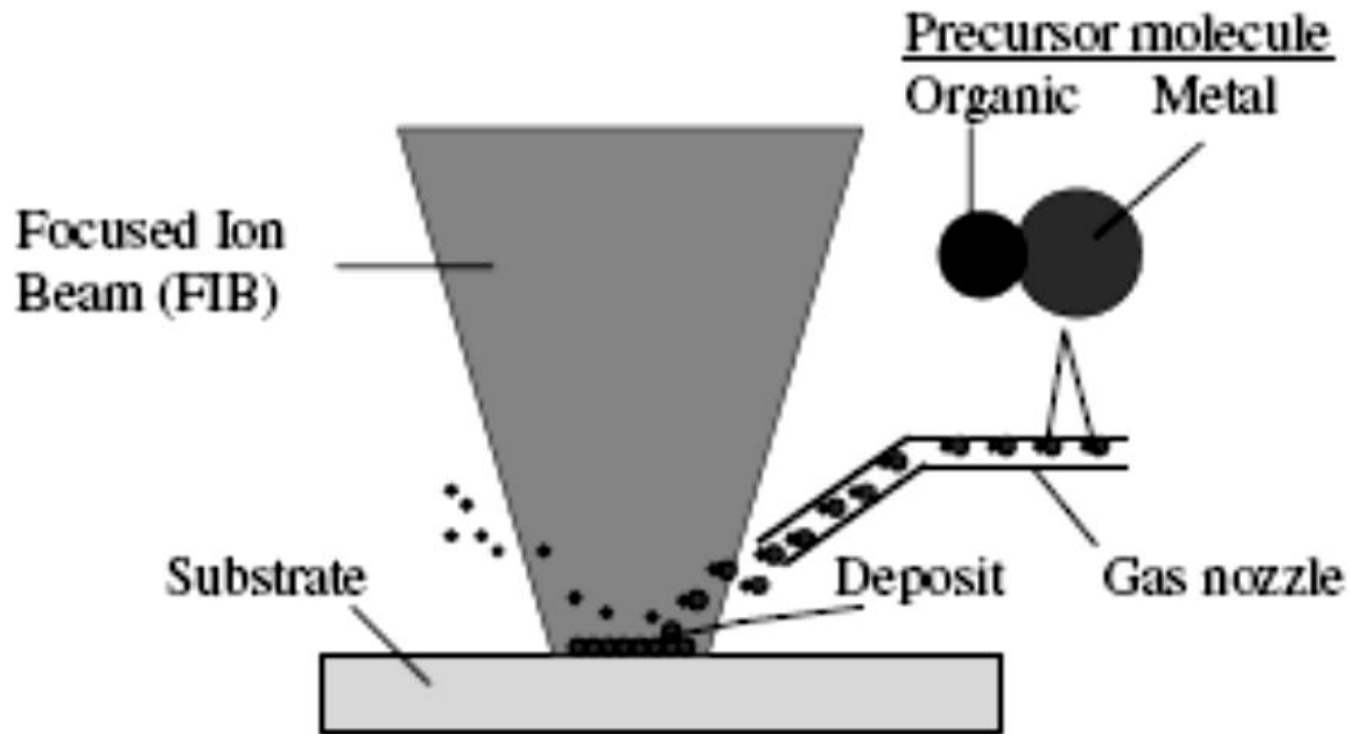
N_2 /atom ratio is 1, Si content 9 at%

Colligon et al TSF 485 (2005) 148-154



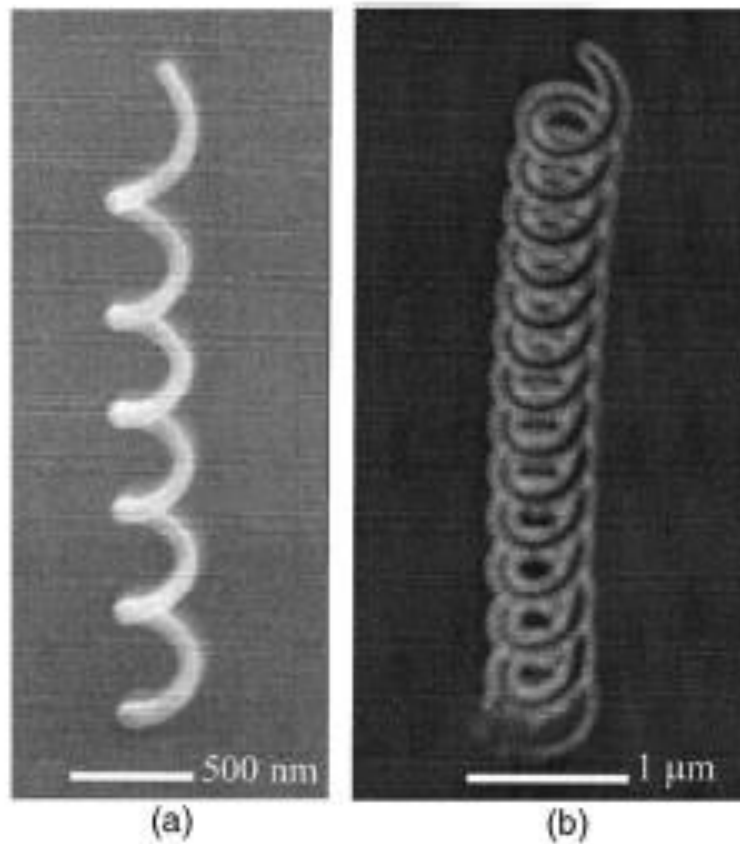
**Ti-Si-N films with 9 at % Si formed using IAD with 400eV N₂ ions;
ion/atom ratio = 1**

Colligon et al TSF 485 (2005) 148-154



Ion beam induced deposition using 98 pA 30keV Ga and $\text{W}(\text{CO})_6$ precursor.

Sadki et al, Physica C 426-431 (1995) 1547-1551

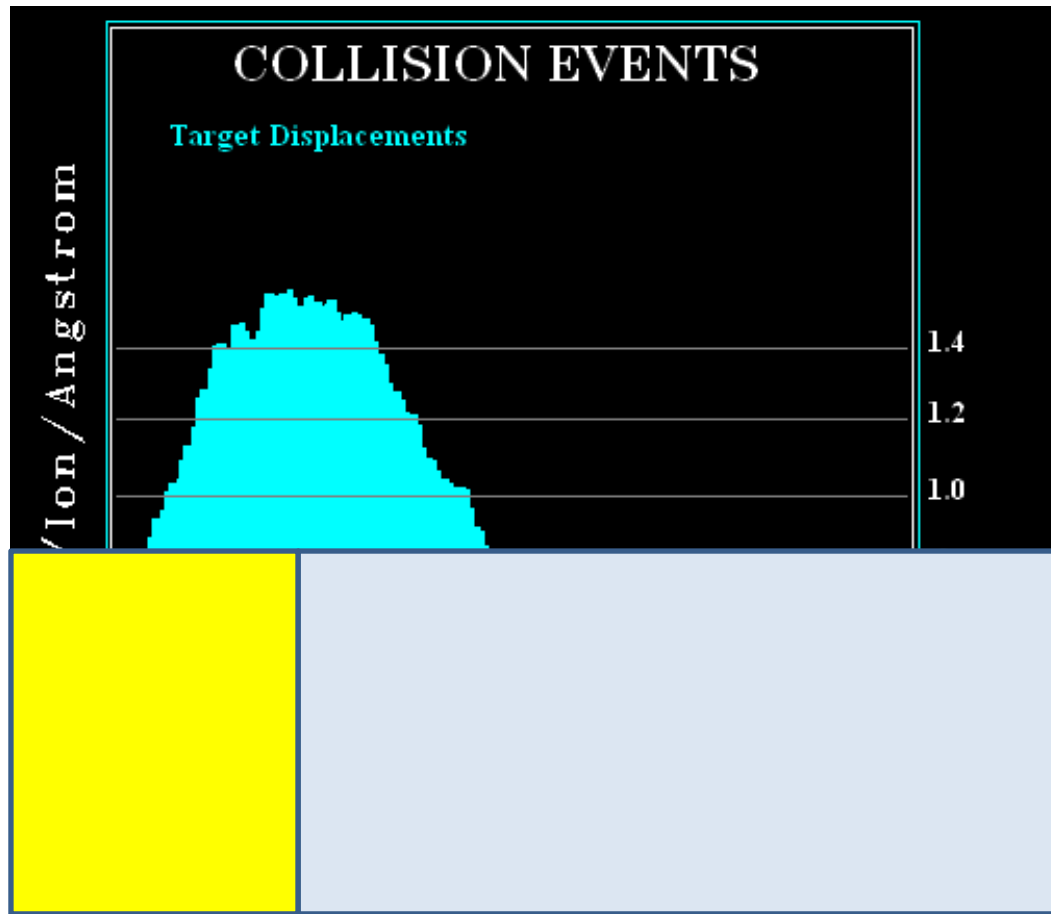


**DLC 380nm coil dia, 130nm wire section springs using penanthrine ($C_{14}H_{10}$) and
1pA 30keV Ga ions**

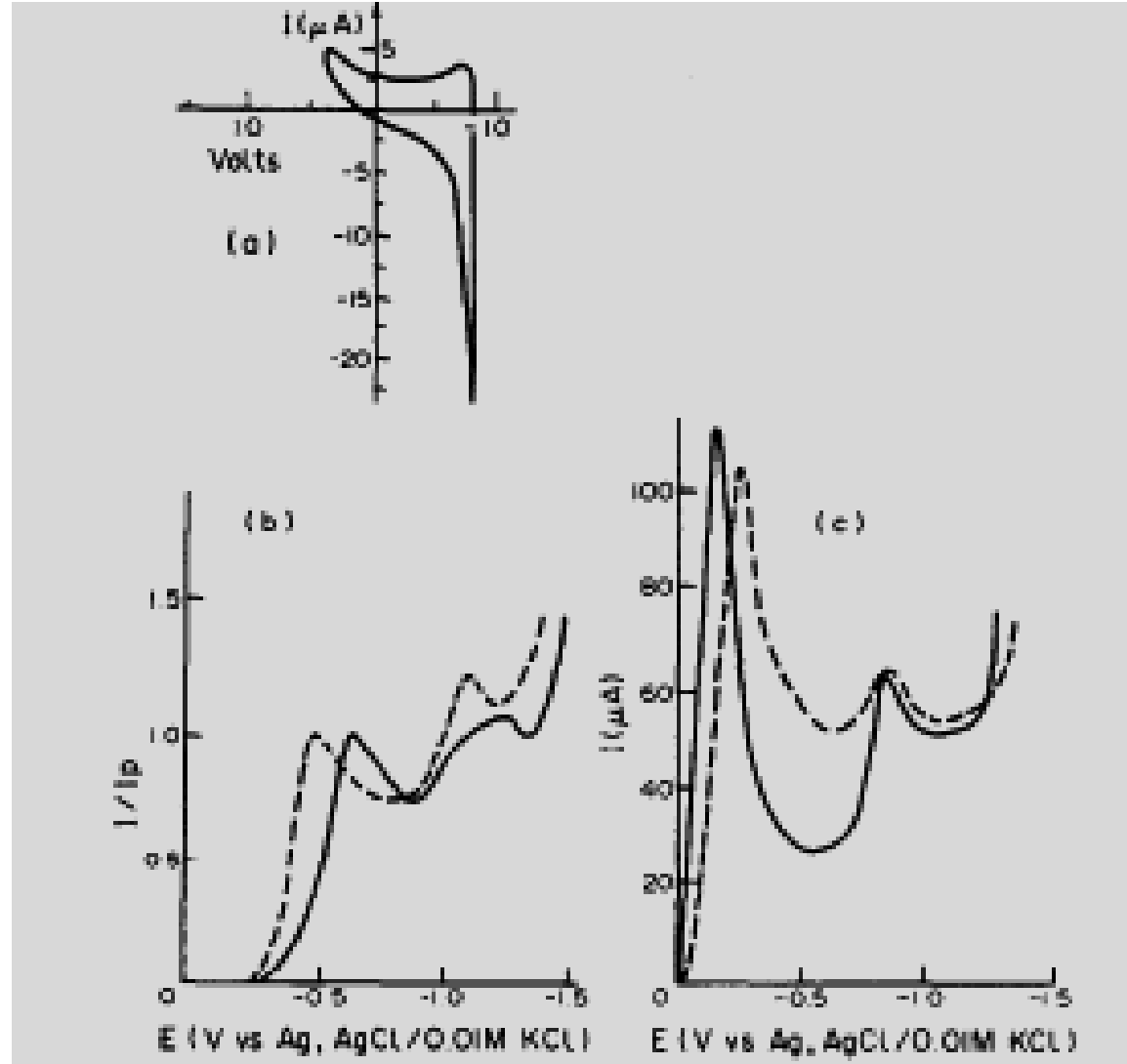
Nakamatsu et al JVST B 23 (6) (2005) 2801-5

DYNAMIC RECOIL MIXING

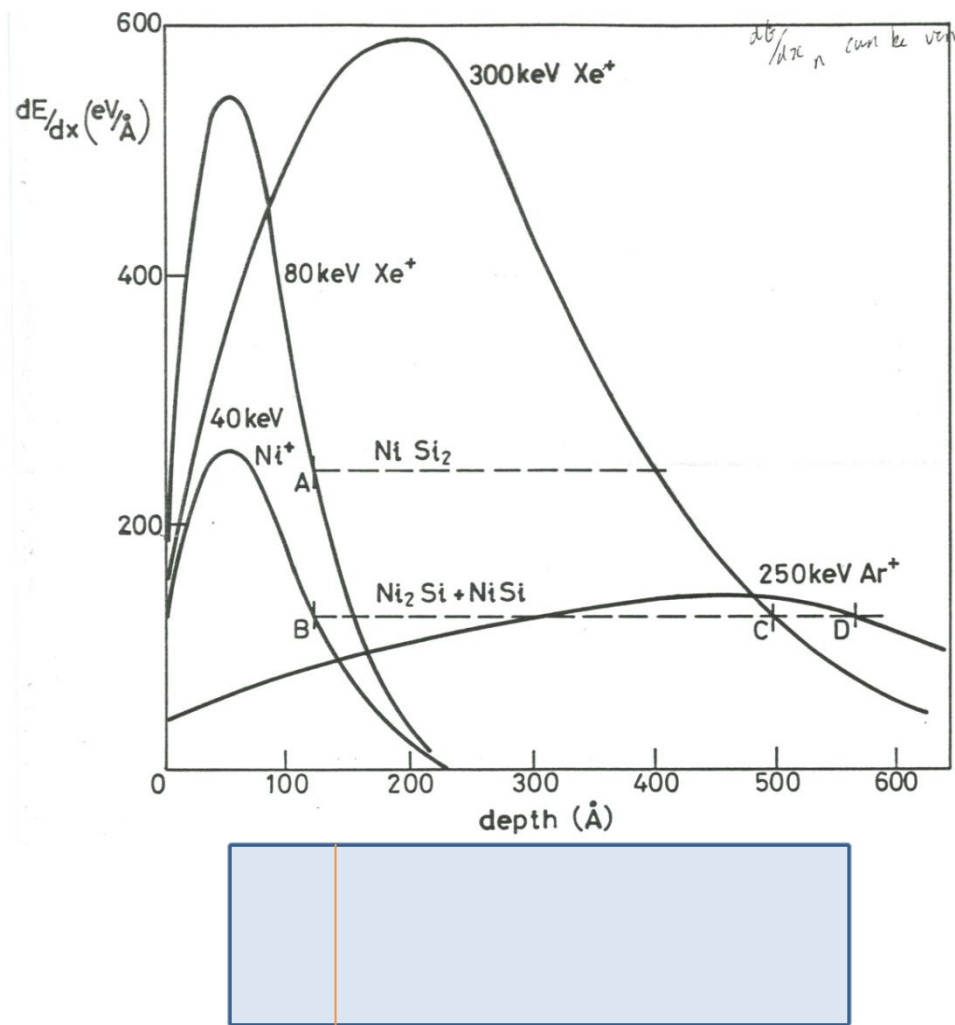
By maintaining a constant thin film of material on a substrate by matching the deposition rate to the re-sputter rate atoms can be recoil implanted into the substrate. Gold was recoil implanted into PET plastic to form a sensor



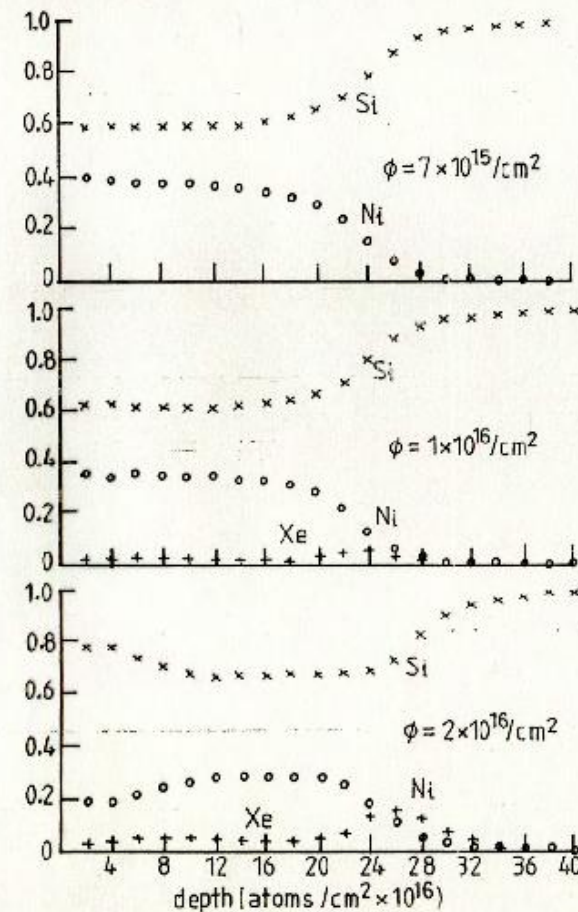
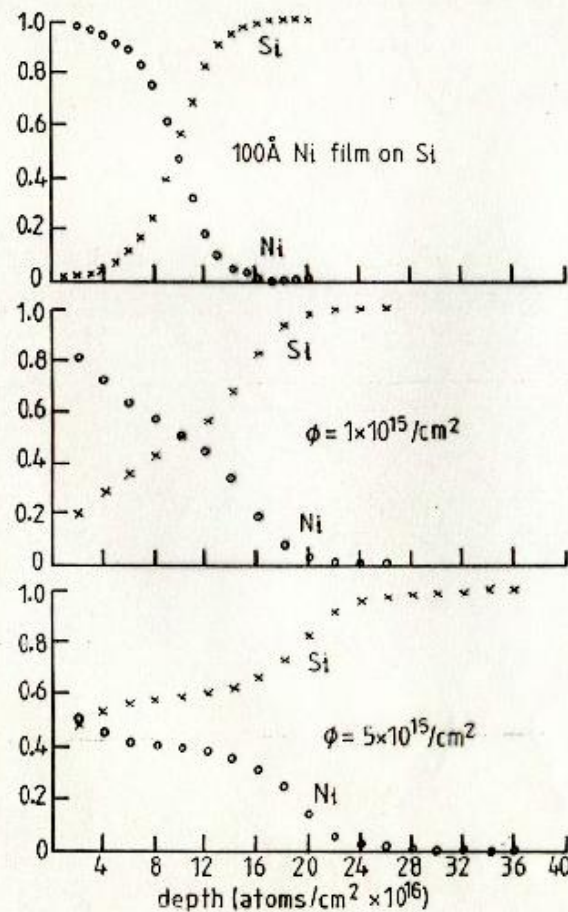
Choose thickness of Au layer so the maximum number of collisions occurs between the gold and the substrate. During bombardment add more gold to replace exactly the amount sputtered. At the end remove surface gold and find gold remains below the substrate surface (Colligon et al, unpublished)



Electrochemical properties of DRM layers punched into PET
 (a) Pt in Ti (0.5M ultrar H_2O_4); (b)--- pure gold;— DRM gold;
 (c) DRM gold lifetime response – original; --- after 12 weeks



By matching the thickness of Ni on Si you can select the energy loss per Ångström at the interface for different ions and energies (e.g. 40keV Ni gives about $120 \text{ eV}/\text{\AA}$ (point B) whereas 80keV Xe gives about $230 \text{ eV}/\text{\AA}$ (point A). Different nickel silicides result



Ni-Si depth profiles formed by 80keV ion bombardment of 10nm Ni on Si. Ion dose increases going down left set from top. Horizontal lines at 0.4 and 0.6 at top right show Ni₂Si₃ has formed

Colligon et al, unpublished

MAX phases are of form $M_{n+1}AX_n$ where n is 1,2 or 3 and depends on the different stacking sequence of the MX block between the A-element layers.

M is Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta

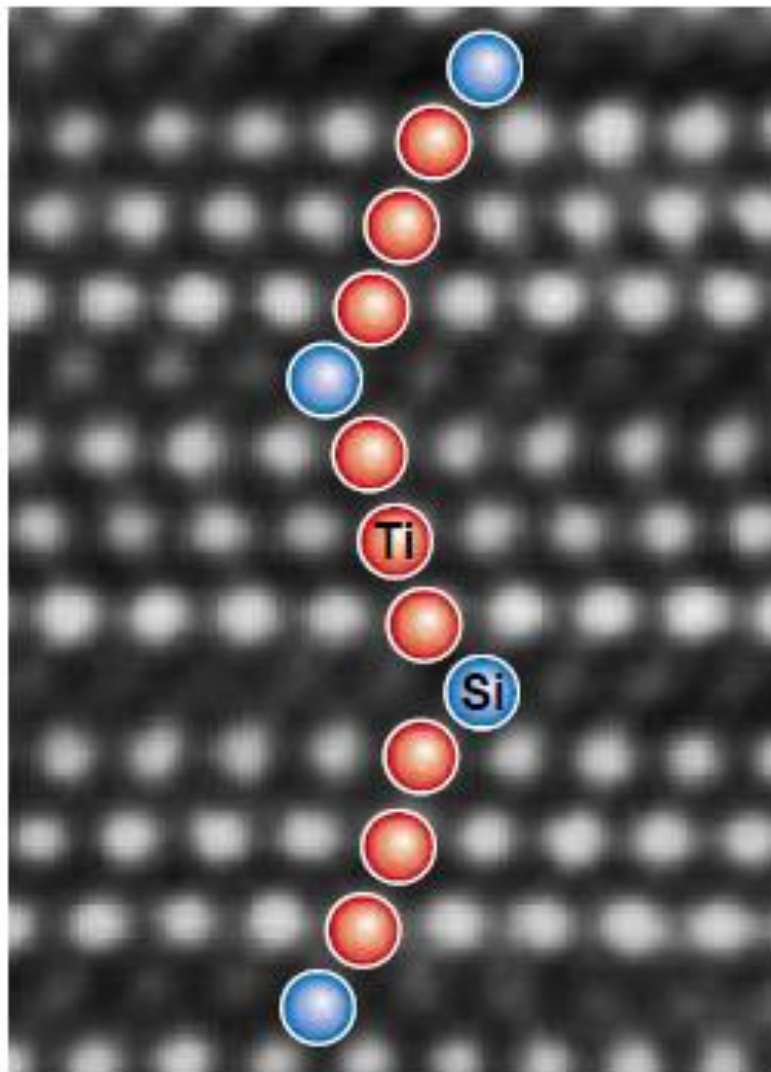
A is group III A or IV A element

**Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Tl, Pb
also can be**

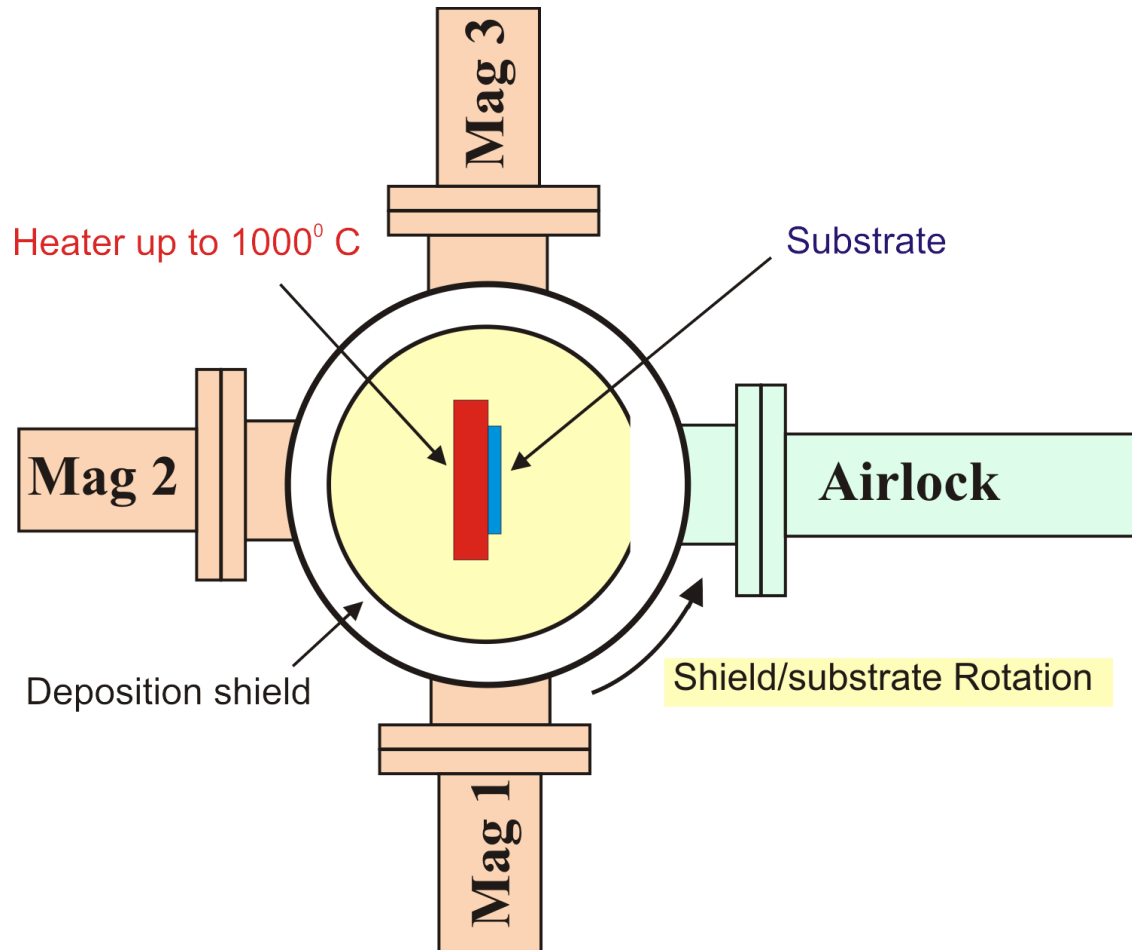
Cd, P, S or As

X is either C o r N

Barsoum showed that highly ductile Ti_3SiC_2 was thermal shock resistant and oxidation resistant even at temperatures in excess of $1000^{\circ}C$.



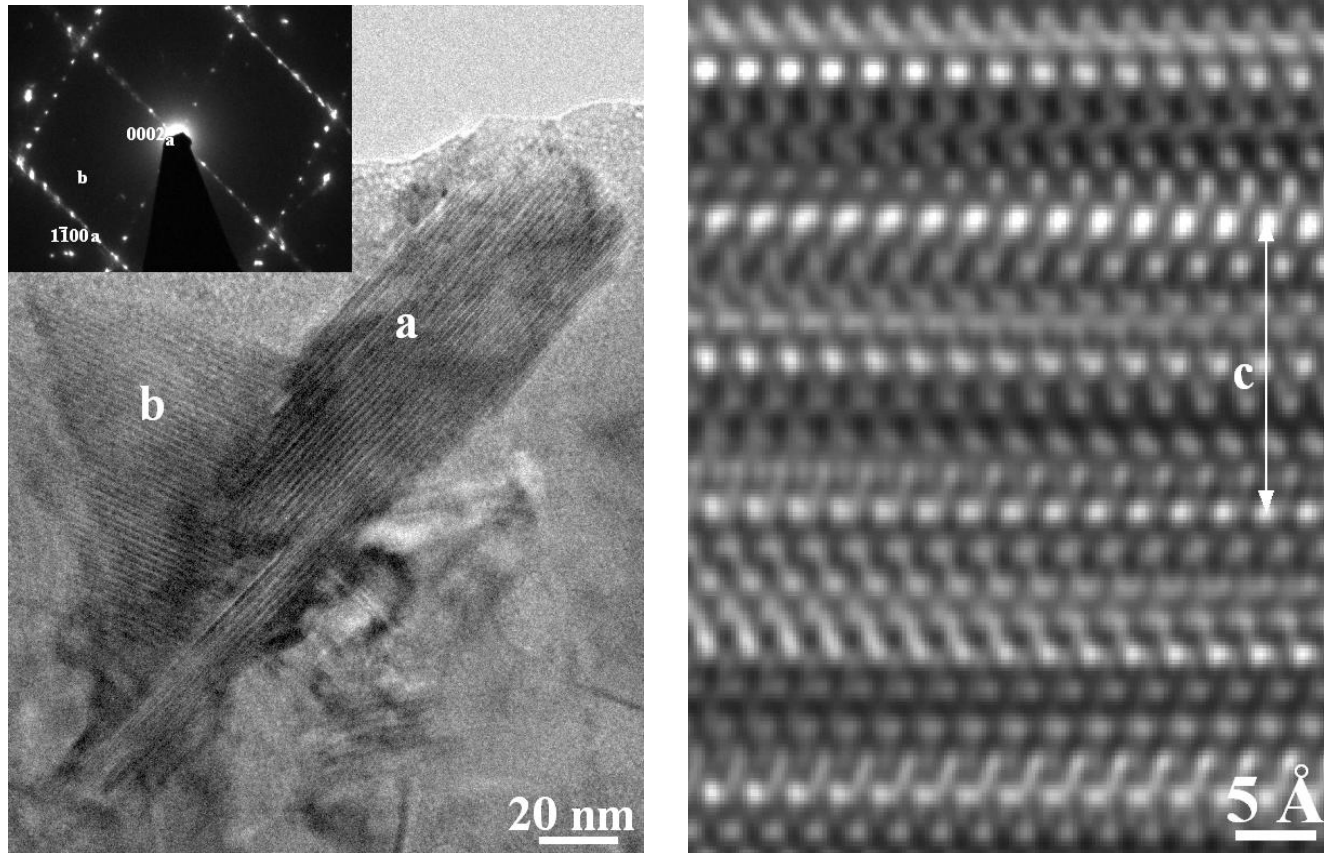
STRUCTURE OF Ti_3SiC_2 : L Farber and I Levin NIST



Sputter Ti (Mag 1), Si (Mag 2) and C (Mag 3) to give layer-by-layer growth on rotating heated substrate

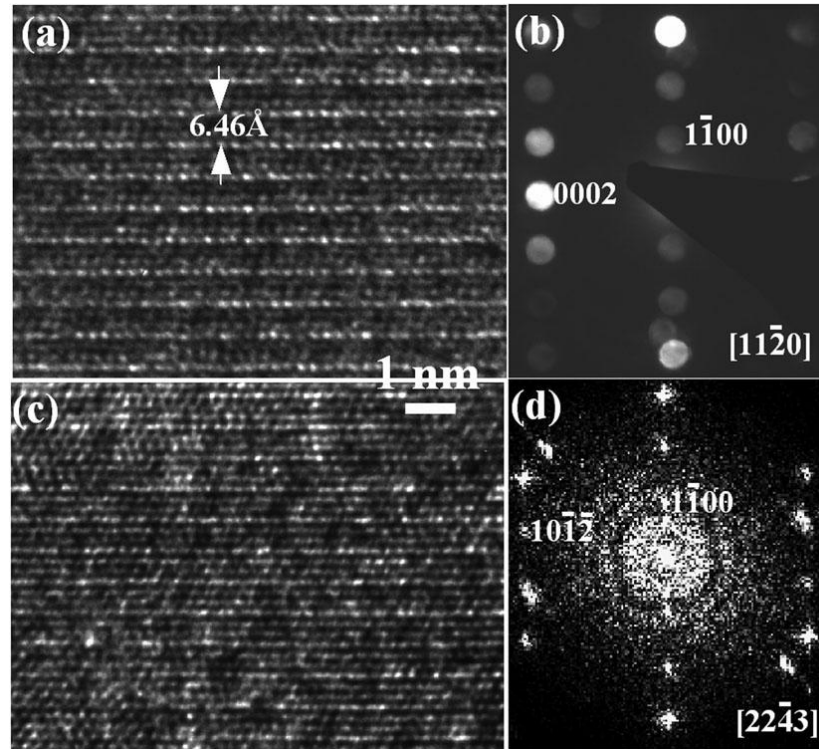
V Vishnyakov, J Lu, P Eklund, L Hultman and J Colligon
Vacuum 93 (2013) 56-59

Atomic fringes for 650^o C



(a) Cross-sectional transmission electron microscopy image, (b) lattice image, and (c) corresponding selected area diffraction electron diffraction pattern from the sample deposited at 650 °C. Lattice spacing $c=1.77\text{nm}$ corresponds with the value for the Ti_3SiC_2 MAX phase

V Vishnyakov, J Lu, P Eklund, L Hultman and J Colligon
Vacuum 93 (2013) 56-59



Ti_3SiC_2 MAX phase

V Vishnyakov, J Lu, P Eklund, J. Colligon and L Hultman et al
 Vacuum 93 (2013) 56-59

SUMMARY

Energy-Assisted Deposition provides control of composition, phase, microstructure, stress and hence improved hardness, temperature stability, radiation resistance, wear and many other coating properties.

Control of deposition conditions is essential, especially impurity content for nanoscale microstructure coatings. In general added energy per atom deposited needs to be of the order 10-20 eV per atom and ion energy about 20-30eV

New developing areas include MAX phases and 2D Maxene

Commercial potential is significant with the world output of products with coatings already exceeding 80 Billion US Dollars per annum

My thanks to many colleagues who have worked with me over the years, in particular Reza Valizadeh, Vladimir Vishnyakov and Hamid Kheyrandish.

Thanks also to the UK funding bodies EPSRC and STFC for valuable support

Last but not least

THANK YOU