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ION IMPLANTATION IN METALS

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ION IMPLANTATION IN METALS

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ABSTRACT

The application of ion beams to metals is rapidly emerging as a promising area of research and technology. This report briefly describes some of the recent advances in the modification and study of the basic properties of metals by ion implantation techniques. Most of the research discussed illustrates some of the new and exciting applications of ion beams to metals which are under active investigation at Sandia Laboratories, Albuquerque.

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I. INTRODUCTION

Ion implantation is being used increasingly to modify and study metals in near surface regions.[1] This application complements the more developed implantation doping of semiconductors. Three very promising new areas of ion implantation in metals are (1) the low temperature production of new metastable materials, (2) the rapid production of specially tailored equilibrium phases for metallurgical research and (3) the rapid simulation of long term radiation damage to reactor materials. Of great importance to the study of ion implantation in metals is the development and application of new near-surface analytical techniques. These include ion backscattering, ion-induced nuclear reactions, channeling lattice-location analysis and imaging field desorption microscopy.

II. METASTABLE MATERIALS

Recently, high flux ion implantations have been used to produce $\lesssim 100\%$ substitutional metallic alloys in the surfaces of single crystals after room temperature or low temperature implantation without further thermal annealing.[2] Figure 1 shows angular scans of single crystal Cu implanted with either Au or W. These results for approximately 3% alloys show almost 100% substitutionality of Au in Cu and almost 90% substitutionality of W in Cu.[2] Since tungsten is very insoluble in Cu, these results demonstrate that metastable solid solutions can be formed by ion implantation without annealing. In fact annealing tends to reduce the substitutionality of the W in the Cu as expected. Although the analysis of such metastable implanted metals is not fully understood there is a rough correlation of increased substitutionality of the implanted ions in Cu with smaller atomic size of the implanted ion.[3]

Very recently ion implantation has been used to form amorphous metal alloys. As a research tool ion implantation should provide a more controlled means of producing these technologically interesting materials than techniques such as "splat cooling." Additional analyses, however, are necessary in order to understand the physical processes involved in the formation of these metastable materials.

Ion implantation is being used extensively in the study of superconductors, both for damage production and for the creation of non-equilibrium phases. As an example, Figure 2 shows the transition temperatures obtained by Stritzker and coworkers[4] in the Pd-H-noble-metal alloys implanted with H to optimum concentrations. Implantations were performed at 4°K to concentrations greater than one H per metal atom, which is far above the equilibrium solubility. These workers conclude that both the H and the noble metal atoms suppress the paramagnetism of the Pd, and they speculate further that the peaks in T_c shown in Fig. 2 correspond to the appearance of soft phonon modes in the metastable phase. Very little information on microstructure is available for these materials. Again, more structural measurements and new insight are required to understand the non-equilibrium alloys made possible by ion implantation.

III. EQUILIBRIUM PHASES

In contrast to the remarkable but not well understood results for non-equilibirum alloys, ion implantation has provided the tools to obtain new, quantitative, and well understood information about equilibrium phases of intermetallic alloys. The preparation of intimate atomic mixtures by ion implantation allows the rapid low-temperature formation of desired phases, which can then be characterized by electron microscopy and diffraction. The use of ion backscattering to continually and non destructively monitor the depth distribution of the implanted atoms to depths beyond the implanted layer permits sensitive determinations of phase diagrams and diffusion rates.

In dilute Be alloys Myers[5] has used ion implantation to prepare specially tailored binary and ternary alloys to study diffusion, solubility and precipitation. These studies provide information at low temperatures and in complex alloys, information not obtainable by other means. Figure 3 gives diffusion coefficients for dilute Cu in Be to values as low as 10^{-15} cm^2/sec. One can also see how the data smoothly fit radiotracer diffusion data[6] at higher temperatures.

Copper implanted into Be at concentrations above the solid solubility was used to obtain solubility measurements.[3] The results are shown in Figure 4. In some cases ion implantation enhanced diffusion has been used to accelerate equilibrium for solubility measurements at very low temperatures. Furthermore, these methods have been successfully extended to ternary alloys of Be and to alloys of Al and Fe.[5]

IV. RADIATION DAMAGE

Ion implantation into metals is important as an experimental technique to simulate both the neutron damage encountered in fast breeder reactors and the surface processes of importance in thermonuclear fusion reactors.[7] The most crucial materials problem in fast breeder reactors at the present time is swelling associated with void formation. The amount of void swelling that takes years to develop in existing steady-state reactors can in principle be produced in hours by charged particle bombardment.[7] In addition ion simulation can be used as a rapid screening tool for low swelling alloy development.

In fusion reactors, plasma contamination by first-wall surface reactions is a problem whose importance is second only to plasma confinement and heating. Helium ion implantation is being used to study the behavior of helium in candidate first-wall materials. Figure 5 gives the depth distribution of implanted He in vanadium as a function of implant temperature. These measurements of He depth profiles show that very little helium is released for samples implanted at 400°C despite the observation of significant surface blistering.

These results illustrate only a small aspect of the important use of ion implantation to study radiation damage in metals. In a more general sense the role that radiation damage plays in the ion implantation process itself is crucial to a fundamental understanding of all applications of ion implantation.

V. NEAR-SURFACE ANALYSIS TECHNIQUES

Equally as important as ion implantation are ion surface analysis techniques such as ion backscattering, ion induced x-rays and nuclear reactions, and ion channeling. For example, by suitably combining these techniques direct determinations of the lattice locations of hydrogen and helium isotopes can be made in single crystal transition metals. Such metals are difficult to investigate by traditional techniques such as neutron diffraction or NMR which require high concentrations throughout the crystal. In contrast the ion channeling technique requires moderately high concentrations only near the surface, and this can be achieved easily using ion implantation. Figure 6 gives angular scans through the

<100> axis for (a) W and (b) Cr for D implanted at 296K.[9] The D(^{3}He,p)^{4}He nuclear reaction was used to detect the implanted D. The analysis indicates the D is in the tetrahedral interstitial site in W and in the octahedral site in Cr.[9]

Simiiar studies have indicated that the lighter gas atoms such as hydrogen and oxygen have been found to occupy well-defined interstitial positions; whereas, the heavier noble gas atoms do not occupy well-defined interstitial or substitutional sites. In the bcc transition metals deuterium is located in tetrahedral sites in W, Cr, and Mo at low temperature and in distorted octahedral sites in Cr and Mo at higher temperatures.[9]

For implanted He in W, multiple He atoms are trapped by lattice vacancies. Complications to the interpretation are changes in lattice location with temperature and upon interaction with radiation produced defects.[9]

In addition to the ion backscattering and ion channeling techniques just discussed, which can give depth distributions with ≈100Å depth resolution and lattice location information of interstitial impurities to ≈0.4Å, a powerful new technique has recently been developed. This technique, known as "Imaging Field-Desorption Mass Spectrometry" is capable of imaging individual atoms,[10] and can measure depth profiles of implanted impurities in the near surface region with monolayer resolution. Figure 7 gives the depth profile of 80 eV D implanted into W. The depth scale is given in terms of the

(110) plane spacing of W (2.2Å) as successive planes of atoms are pulse field evaporated and the ion masses determined by time of flight mass spectroscopy. Not only is the depth distribution of the implanted D resolved, but the large penetration depth indicates that the D has been channeled into the W single crystal. The oscillations that are revealed are believed to be sensitively related to the surface lattice location of C and O impurity atoms. Also resolved is the depth distribution of the C and O which are recoil implanted and channeled into the W. It is believed that the Imaging Field Desorption Mass Spectrometer is the only instrument capable of measuring such low energy ion implantation depth distributions. Such recoil effects are important for ion implantation in semiconductors and for fusion reactor first wall studies.

VI. SUMMARY

Ion implantation in metals is a rapidly developing field with several exciting sub fields. The development of new techniques and insights guarantee continued rapid progress and numerous applications.

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FIGURE CAPTIONS

FIG. 1 <110> channeling angular scans for 1.8 MeV He backscattered from single crystal Cu implanted with Au or W (Ref. 2). Agreement of curves for host and implant atoms indicates degree of substitutionality.

FIG. 2 Superconducting transition temperature in H-implanted Pd-H-noble metal alloys (Ref. 4).

FIG. 3 Temperature dependence of the diffusion coefficient for dilute Cu in Be single crystals for both <u>a</u> and <u>c</u> axes (Ref. 5). Open symbols ion implantation work. Closed symbols from radiotracer measurements (Ref. 6).

FIG. 4 Solubility of Cu in Be (Ref. 3). The open diamonds are the implantation data and the solid symbols are previous results by other techniques.

FIG. 5 Measured depth distribution of 80 keV implanted He in V at implant temperatures indicated. $R_p = 0.3$ μm (Ref. 8).

FIG. 6 Angular scans through the <100> axis for (a) W and (b) Cr for 3×10^{15} cm^{-2} 30 and 15 keV D implants, respectively at 296K. A 750 keV ^{3}He analysis beam was used; circles correspond to backscattered yields for W and Cr, and triangles correspond to proton nuclear reaction yields from D (Ref. 9).

FIG. 7 Depth profiles of C^{2+}, C^{+}, O, and D in the near surface region of W following implantation with 80 eV deuterium at 300°K. Depth measured in discrete steps determined by (110) interlayer spacing, 2.23Å.

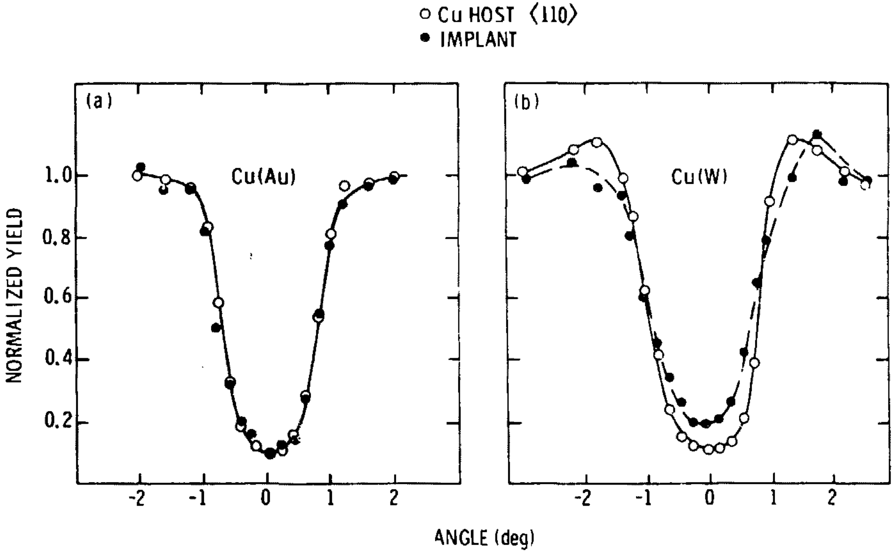

○ Cu HOST ⟨110⟩
● IMPLANT
(a)
Cu(Au)
(b)
Cu(W)
NORMALIZED YIELD
1.0
0.8
0.6
0.4
0.2
-2
-1
0
1
2
ANGLE (deg)

FIG. 1

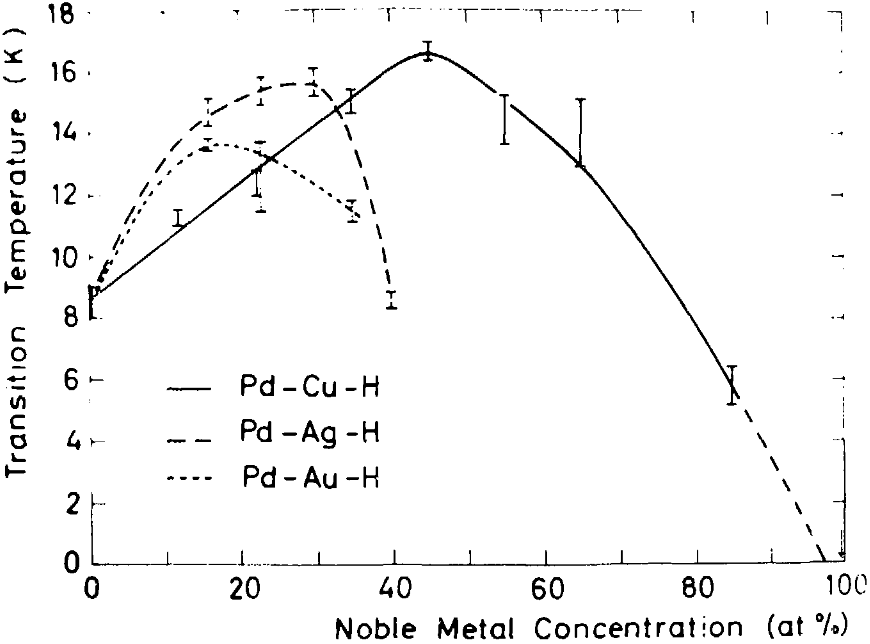

Transition Temperature (K)
18
16
14
12
10
8
6
4
2
0
0
20
40
60
80
100
Noble Metal Concentration (at %)
Pd – Cu – H
Pd – Ag – H
Pd – Au – H

FIG. 2

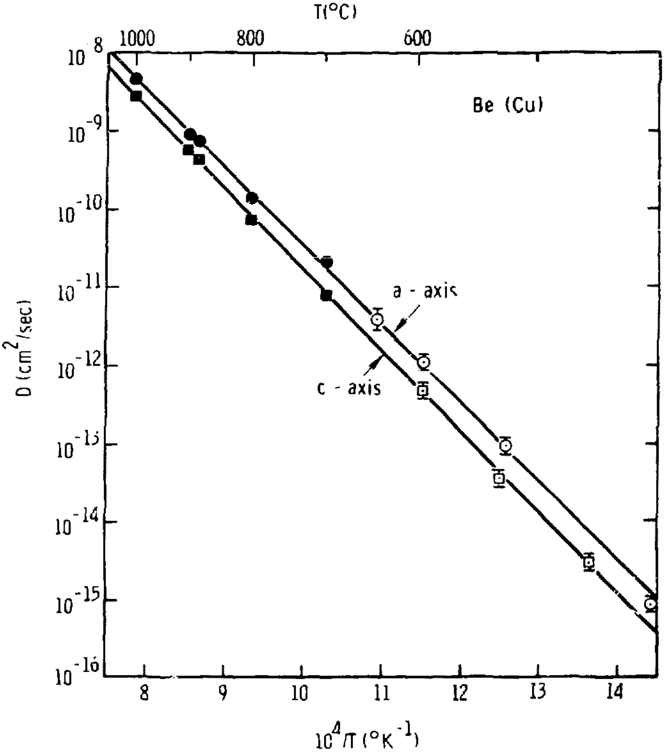
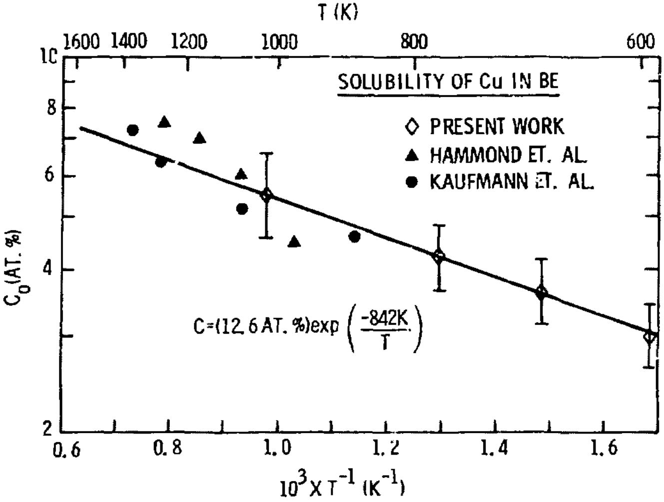

T(°C)
1000
800
600
Be (Cu)
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
D (cm^2/sec)
a - axis
c - axis
8
9
10
11
12
13
14
10^4/T (°K^{-1})

FIG. 3



T (K)
1600
1400
1200
1000
800
600
10
8
6
4
2
SOLUBILITY OF Cu IN BE
◇ PRESENT WORK
▲ HAMMOND ET. AL.
● KAUFMANN ET. AL.
C_0 (AT. %)
$C=(12.6\ \text{AT.}\ \%)\exp\left(\frac{-842\text{K}}{T}\right)$
0.6
0.8
1.0
1.2
1.4
1.6
$10^3 \times T^{-1}\ (K^{-1})$

FIG. 4

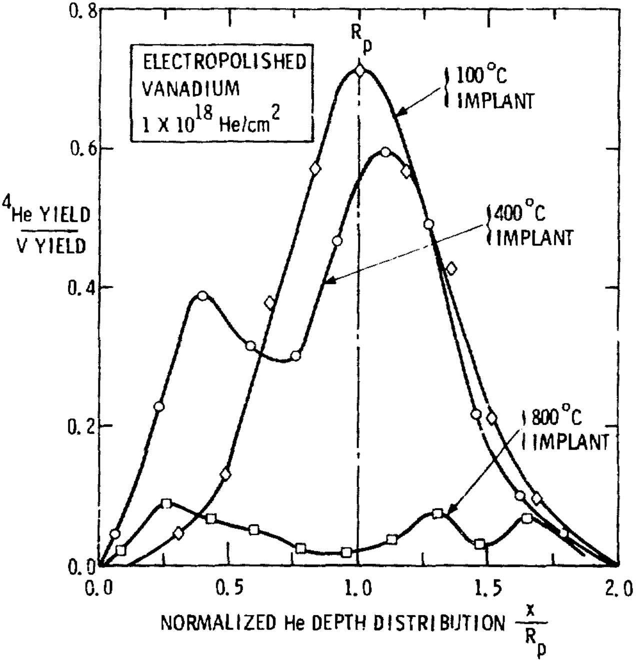

0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
^{4}He YIELD / V YIELD
NORMALIZED He DEPTH DISTRIBUTION $\frac{x}{R_p}$
R_p
ELECTROPOLISHED
VANADIUM
1 X 10^{18} He/cm^2
100 °C IMPLANT
400 °C IMPLANT
800 °C IMPLANT

FIG. 5

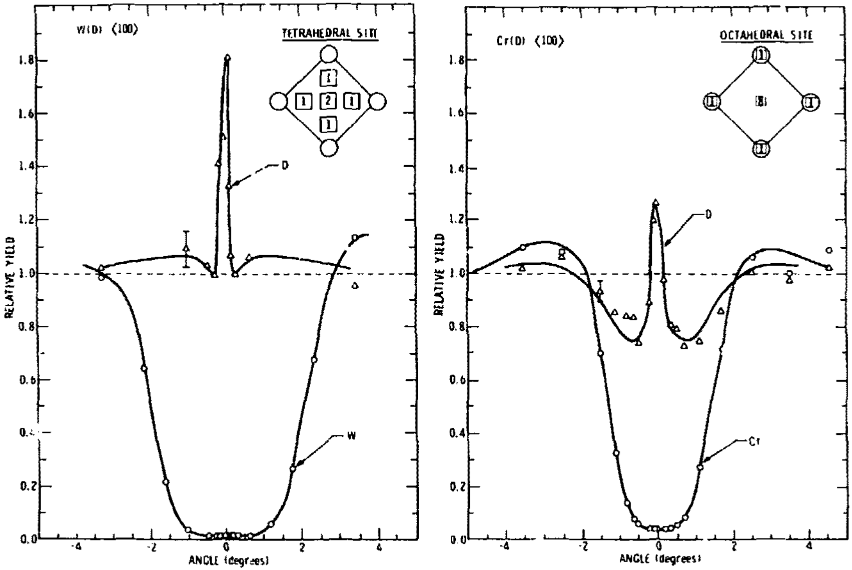

W(D) ⟨100⟩
TETRAHEDRAL SITE
1
1
2
1
1
D
W
RELATIVE YIELD
ANGLE (degrees)
Cr(D) ⟨100⟩
OCTAHEDRAL SITE
1
1
1
1
8
D
Cr
RELATIVE YIELD
ANGLE (degrees)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
-4
-2
0
2
4

FIG. 6

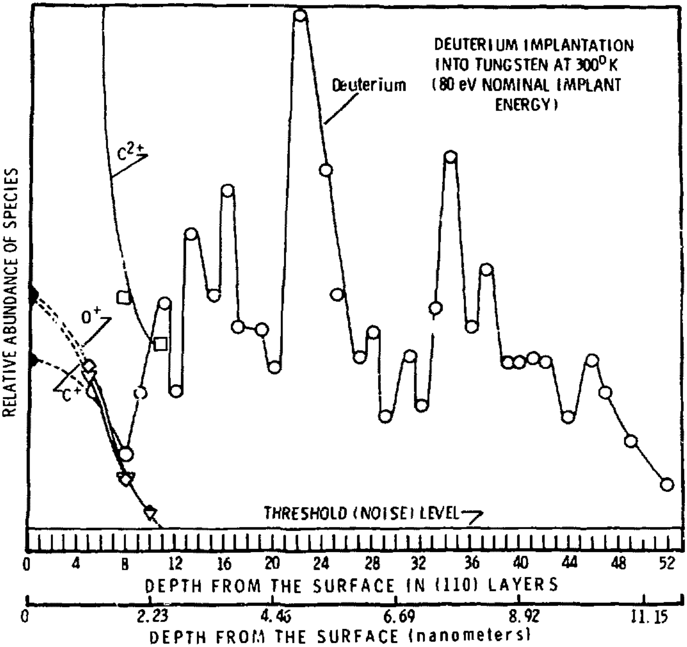

DEUTERIUM IMPLANTATION INTO TUNGSTEN AT 300° K (80 eV NOMINAL IMPLANT ENERGY)
Deuterium
C^{2+}
O^{+}
C^{+}
THRESHOLD (NOISE) LEVEL
RELATIVE ABUNDANCE OF SPECIES
0
4
8
12
16
20
24
28
32
36
40
44
48
52
DEPTH FROM THE SURFACE IN (110) LAYERS
0
2.23
4.46
6.69
8.92
11.15
DEPTH FROM THE SURFACE (nanometers)

FIG. 7