Nucleation of body-centered-cubic tantalum films with a thin niobium underlayer

D. W. Face and D. E. Prober
Section of Applied Physics, Yale University, New Haven, Connecticut 06520

(Received 2 March 1987; accepted 21 June 1987)

We discuss the structural and electrical properties of high-quality Ta films prepared by ion beam sputter deposition. The Ta films grow in two different crystal structures, body-centered-cubic (bcc) or tetragonal (β-Ta), depending on the substrate preparation and sputtering conditions. Ta films deposited on a thin (> 0.3 nm) Nb underlayer grow in the bcc crystal structure with properties approaching those of clean bulk polycrystalline material. The bcc-Ta films have a superconducting transition temperature of 4.3 K and a low-temperature (10 K) resistivity ρ ~ 6 μΩ cm. Ta films deposited without a Nb underlayer on Si substrates always grow in the tetragonal (β-Ta) structure. The β-Ta films do not superconduct above 1 K and have a high resistivity ρ ~ 150 μΩ cm. X-ray diffraction and transmission electron microscope studies of both Ta structures are presented. Both bcc-Ta and β-Ta films are deposited on room-temperature substrates. This allows either type of film to be easily patterned by standard photolithography methods.

I. INTRODUCTION

Tantalum films are important in a number of applications such as thin-film capacitors and resistors. The chemical stability and robust mechanical properties of Ta make it a particularly desirable material. The nearly ideal, low-loss, dielectric properties of tantalum oxide (Ta₂O₅) layers grown on Ta films are also very desirable. Superconducting tunnel junctions produced with Ta₂O₅ tunnel barriers on Ta base electrodes are also found to have nearly ideal characteristics, which is important for producing quantum-limited millimeter-wave receivers.

It is well known that Ta films can be produced in two different crystallographic phases, body-centered-cubic (bcc) and tetragonal (β-Ta), which have very different electrical properties. The bcc phase of Ta is easily produced in bulk single-crystal form and its properties have been well studied. The bcc-Ta phase has a superconducting transition temperature Tc of 4.4 K and a room-temperature resistivity of ρ ~ 13.6 μΩ cm. On the other hand, β-Ta is less well studied and it appears to be formed most easily as a thin film. There is only one report of β-Ta grown in the bulk form. Although the reported values of resistivity for pure β-Ta vary somewhat, a value of ρ ~ 150 μΩ cm is generally found. β-Ta has a superconducting transition temperature Tc of 0.5 K.

The exact mechanisms that lead to the formation of bcc-Ta or β-Ta are not clearly identified even though a large number of papers have been published on the subject. Several authors have found that the nature of the substrate has a large effect on the nucleation of either β-Ta or bcc-Ta. Vacuum system impurities have also been found to have a large effect on the nucleation and growth of Ta films.

In a previous publication, we reported on the properties of ion-beam-deposited Nb and Ta films. We found that the crystal structure of Ta films grown on room-temperature substrates could be easily and reproducibly controlled by the deposition of a thin (> 0.3 nm) Nb underlayer. This ability to control the structure of our Ta films has been of great importance in our recent work on high current density, Jc ~ 10⁶ A/cm², Ta/Ta₂O₅/PbBi tunnel junctions with low leakage currents. The fact that the Nb underlayer technique works on room-temperature substrates is important in that one can use photolithography liftoff for high-resolution patterning. Thermal degradation of other layers and interfaces is also avoided.

In this paper we present a more detailed description of both the bcc and β-Ta films including x-ray diffraction and transmission electron microscope (TEM) studies. These studies reveal that the crystal structure of our films is critically dependent on the initial nucleation process. Although we have not specifically investigated the microscopic mechanisms that cause the nucleation of bcc-Ta or β-Ta, we believe that this paper will be useful as a practical and reliable guide for others who wish to control the characteristics of Ta films.

The close lattice match between bcc-Ta and Nb (also bcc) suggests the importance of epitaxial growth. Once a particular phase, β or bcc, is nucleated, it continues to grow with the same crystal structure unless the sputtering conditions are changed. The x-ray diffraction results are used to estimate the compressive stress in our bcc-Ta films.

II. EXPERIMENTAL PROCEDURES

The ion beam sputtering system used in this work employs a Kaufman ion source and has been described in a previous publication. The standard operating conditions use a beam energy of 1500 eV and a beam current of 35 mA, with a chamber pressure of ~2.3 × 10⁻² Pa of xenon gas (> 99.99% pure). The ion beam characteristics during deposition were always very stable (variations < 3%). These sputtering conditions produced a deposition rate of 0.24 nm/s for Nb films and 0.27 nm/s for Ta films.

An initial predeposition sputter period of typically 60 min was always used to allow the source to equilibrate and to provide a layer of freshly sputtered Nb or Ta on a liquid nitrogen (LN₂) cold shield. This sputtered layer acts as a
good getter for impurities in the vacuum system. The $T_c$'s of Nb and Ta films were 9.1 and 4.3 K, respectively (see Table I). These $T_c$ values are within 2% of their respective bulk values and demonstrate the high purity of films produced by ion beam sputtering. The ~0.1 K depression from bulk $T_c$ values we observe is likely due to a combination of disorder, impurities, and stress in our polycrystalline films.

The multiple-target holder used in our system can rotate any one of four different water-cooled targets (Nb, Ta, Al, Si, etc.) under the beam. We used 10-cm-diam Nb and Ta (99.9 + % purity) targets, the centers of which were ~15 cm from the ion source when sputtering. The water cooling kept the temperature rise of the target during sputtering to <30 °C.

For almost all of the films studied, we have used 6.35×6.35 mm Si(100) substrates which were cleaned ultrasonically in solvents and blown dry. The films prepared for TEM study were deposited on a thin (~ 30 nm) amorphous carbon film which was suspended on a standard 200-mesh TEM grid.

Electron diffraction, transmission electron microscopy, and scanning transmission electron microscopy (STEM) were all performed on a JEOL 100CX Temscan. X-ray diffraction measurements were made using a standard x-ray diffractometer with a Cu $K_\alpha$ x-ray source. Positions of the Nb and Ta peaks on the diffractometer traces were referenced to the silicon substrate peaks, allowing an absolute accuracy of ±0.05°.

III. RESULTS

A. β-Ta films

We found that Ta films deposited on clean (room air oxidized) Si substrates always grew in the well-known tetragonal (β-Ta) crystal structure [see Fig. 1(a)]. The observation of a very strong (200) x-ray diffraction peak in Fig. 1(a) (compared to the 211 reflection) indicates a strong degree of preferred orientation in the (100) direction. This observation is consistent with that of other workers. In order to search for any evidence of bcc-Ta in our β-Ta films, we have performed additional off-axis x-ray scans to search for bcc-Ta reflections. No evidence of bcc-Ta was found.

<table>
<thead>
<tr>
<th>Film thickness*</th>
<th>Nb</th>
<th>Ta</th>
<th>bcc lattice constant</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk Nb</td>
<td>3.301</td>
<td>3.353</td>
<td>4.0</td>
<td>3.86</td>
</tr>
<tr>
<td>25-2</td>
<td>3.303</td>
<td>2400</td>
<td>6.1</td>
<td>3.23</td>
</tr>
<tr>
<td>210-4</td>
<td>30</td>
<td>2400</td>
<td>3.324</td>
<td>7.2</td>
</tr>
<tr>
<td>210-1</td>
<td>3</td>
<td>2400</td>
<td>3.324</td>
<td>151</td>
</tr>
</tbody>
</table>

Fig. 1. (a) X-ray (Cu $K_\alpha$) diffractometer scan from a 240-nm Ta film deposited on a Si substrate without a Nb underlayer. This film has the β-Ta crystal structure (tetragonal). (b) X-ray diffractometer scan of a 240-nm Ta film deposited on a 10-nm Nb underlayer to nucleate the bcc (superconducting) phase of Ta.

β-Ta also formed when the films were deposited on amorphous carbon substrates (for TEM study) as shown in Fig. 2(a). The grain size is ~30 nm. The uniform diffraction rings indicate that β-Ta crystallites are randomly oriented with respect to rotations in the plane of the film.

In order to produce a clean (oxide-free) Si surface before Ta deposition, we also used the multiple-target holder to sputter deposit an underlayer of amorphous Si ($\alpha$-Si). This was accomplished by depositing a layer of $\alpha$-Si ~35 nm thick and then immediately (within ~1 s) rotating the target holder to the Ta position without turning off the beam or closing the shutter. Ta films deposited on the fresh amorphous Si layer also grew in the β-Ta structure. The electrical properties of β-Ta films are presented in Table I. The β-Ta films did not become superconducting above 1.5 K, which is consistent with the published $T_c$ of 0.5 K for the β-Ta phase.

B. bcc-Ta films

In order to promote the formation of Ta in the bcc phase (bulk $T_c = 4.4$ K) we have ion beam deposited a layer of Nb onto the Si substrates just before depositing the Ta. Nb was

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*Ta films were deposited on Nb to nucleate bcc-Ta (see text).

*bRRR is the residual resistance ratio, i.e., the ratio of the room-temperature resistivity to the low-temperature (10 K) resistivity.
thought to be a favorable underlayer material because it has the same crystal structure as bcc-Ta and a lattice mismatch of $<0.1\%$. The Nb underlayer (0.3–60 nm thick) was prepared by briefly sputtering a layer of Nb and then quickly (within $\sim1$ s) rotating the target holder from Nb to Ta. Nb underlayers of 0.3 and 1.0 nm caused a dramatic decrease in the amount of $\beta$-Ta, by a factor of more than 100. Ta films on Nb underlayers thicker than 1.0 nm showed no detectable amount of $\beta$-Ta, as shown in Fig. 1(b). Nb underlayers of all thicknesses produced a large increase in the amount of bcc-Ta as inferred from $T_c$ and low-temperature resistivity. The x-ray scan in Fig. 1(b) also shows a strong degree of (110) texturing. The Ta film data are summarized in Table I.

We have also used the Nb underlayer technique to nucleate Ta in the bcc structure on amorphous carbon substrates. Figure 2(b) shows a TEM micrograph of a 30-nm-thick bcc-Ta film on a 3.0-nm Nb underlayer. From this micrograph, we find an average grain size of $\sim15$ nm which is about a factor of 2 smaller than that found for $\beta$-Ta in Fig. 2(a). A 15-nm grain size is consistent with the width of the (110) x-ray diffraction peak in Fig. 1(b). By assuming a constant $\rho l$ product for Ta of $5.9 \times 10^{-6} \mu\Omega \cdot \text{cm}^2$ (Ref. 9) and using our measured resistivity of $\rho \sim 6 \mu\Omega \cdot \text{cm}$, we calculate an electron mean free path of $\sim10$ nm. This indicates that most of the scattering is due to the grain boundaries in bcc-Ta films.

During one unusual deposition, a small amount of water vapor leaked into the system while switching from the Nb to the Ta target. This was caused by a small leak in the water cooling lines for the target. This leak created a partial pressure of water vapor in the sputtering environment of 5 to $10 \times 10^{-3}$ Pa for a period of $\sim5$ s. The presence of the water vapor (and its possible reaction with the Nb surface) caused the Ta film to grow in the $\beta$-Ta structure rather than the intended bcc structure. This demonstrates the sensitive nature of the nucleation and growth process for Ta films.

**IV. DISCUSSION**

The strong influence of the substrate on the nucleation of $\beta$-Ta has been previously observed by other workers. Our findings suggest that the thin Nb underlayer is modifying the substrate surface to provide a surface that favors the formation of the bcc phase of Ta. There may be a propensity for bcc-Ta growth on Nb due to the close lattice match of bcc-Ta and Nb (within 0.1\%). Our findings are also consistent with the hypothesis of Feinstein that the presence of O or OH, formed by the reaction of H$_2$O with the surface oxide favors the nucleation of $\beta$-Ta. If the O or OH on the surface is important, the Nb underlayer could then be reacting with this surface and neutralizing the effect of the O and OH. The fact that $\beta$-Ta was also nucleated on clean a-Si, however, demonstrates that other surfaces (that are quite likely free of O and OH on the surface) can also nucleate $\beta$-Ta. For example, a tantalum silicide layer formed during the initial stages of Ta deposition may favor the nucleation of $\beta$-Ta. In any case, the thin Nb underlayer is a very convenient way to obtain the bcc phase of Ta without substrate heating.

The origin of the high resistivity ($\rho \sim 150 \mu\Omega \cdot \text{cm}$) of $\beta$-Ta has not been clearly established. Although the weak temperature dependence and large value of resistivity observed for $\beta$-Ta are usually indicative of a very disordered material, our x-ray diffraction and TEM studies show that $\beta$-Ta is not strongly disordered. In fact, the grain size of the $\beta$-Ta films is larger than that of bcc-Ta which has a much lower resistivity. The low level of impurities in our films, as judged by nearly bulk properties of our bcc-Ta films and from energy dispersive x-ray analysis, appears to rule out any model based on intergranular tunneling. Clearly, more work is required to properly understand the electrical properties of $\beta$-Ta.

The expanded lattice constant (relative to the bulk) observed in our bcc-Ta films is indicative of compressive stress in the plane of the film. Our x-ray diffraction technique measures the distance between lattice planes that are parallel to the substrate and is therefore sensitive to this lattice expansion.

We have used the measured lattice expansion to make an estimate of the amount of compressive stress in our films by performing a simple bulk calculation. This calculation assumes that compressive stress in the $X$–$Y$ plane will cause an expansion of the crystalline lattice plane spacing in the $Z$
direction (i.e., the unit cell will be distorted from bcc). The ratio of the strain in the \( Z \) direction (\( \delta Z / Z \)) to the strain in the \( X \) or \( Y \) direction (\( \delta L / L \)) is given by the Poisson ratio, \( \left( \delta Z / Z \right) / \left( \delta L / L \right) = \nu \), \( (1) \)

where the stress is related to the strain through the Young's modulus, \( \left( \delta L / L \right) / F = Y \). \( (2) \)

For Ta, \( Y \approx 1.86 \times 10^{-12} \) dyne \( \cdot \) cm \(^{-1} \) and the observed \( \delta Z / Z \) from \( a_0 \) in Table I is \( \left[ \delta Z / Z = (3.328 \ \text{Å} - 3.303 \ \text{Å}) / 3.303 \ \text{Å} = 7.6 \times 10^{-3} \right] \) which gives a compressive stress of \( \approx 1.2 \times 10^{10} \) dyn/cm\(^2\). This value of compressive stress is close to that measured by others \(^1\) for sputtered Ta films.

V. CONCLUSIONS

In summary, we have found that the crystal structure of Ta films is critically dependent on the initial nucleation process. Ta films deposited directly on room-temperature Si substrates grow in the tetragonal (\( \beta \)-Ta) crystal structure. \( \beta \)-Ta also grows on amorphous C and amorphous Si substrates. The initial deposition of a thin Nb underlayer, however, causes the Ta films to grow in the bcc crystal structure. This simple underlayer technique allows the choice of one phase or the other without the use of substrate heating or a change of sputtering conditions. The electrical transport properties of Ta films formed in both structures have been studied and are seen to approach the properties of the bulk material. X-ray diffraction studies of bcc-Ta indicate a compressive stress of \( \approx 1.2 \times 10^{10} \) dyn/cm\(^2\) in the plane of the film.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical advice and assistance of S. T. Ruggiero and E. K. Track. We thank P. Male of the Section of Cell Biology at Yale for assistance with the TEM studies. We also thank W. D. Westwood and J. M. Rowell for several useful discussions regarding tantalum thin films. This research was supported by NSF Grants No. ECS-8305000 and No. ECS-8604350 and ONR Contract No. N00014-80-C-0855.


\(^{11}\) TEM grids were obtained from Ernest F. Fullam, Inc., Schenectady, NY, 12301.


