Effect of UV radiation on the growth and breakdown voltage of anodic oxide films on niobium

Sanjeev Makcn*, Mohinder Singh, K C Kalra & K C Singh
Department of Chemistry, Maharshi Dayanand University, Rohtak 124 001 (India)
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Formation rates of anodic Nb₂O₅ films grown under galvanostatic conditions decrease in the presence of UV radiation, unlike those grown in the absence of UV radiation. This may be due to the development of a positive space charge near the solution/oxide interface which is responsible for an increase in electronic current in the film during its formation. Value of breakdown voltage also increases in the presence of UV radiations. The effect of current density and resistivity of the solution upon the breakdown voltage, both in the present and absence of UV radiation, is discussed in terms of Ikonopisov theory of breakdown voltage.

A considerable interest has been witnessed in the recent years in the studies of growth and electrical breakdown during the anodization of niobium[1-4]. The phenomenon is important both for electrolytic capacitor industry and for anodization in general. The formation rate of anodic oxide films on Ta[5-7] and Al[8] is enhanced by UV radiation, which also causes permanent structural changes. These changes modify the properties of photogrown oxide films as compared to those grown in natural light. In order to see how oxidation of niobium, a typical valve metal, would be affected in the presence of UV radiation, the present work has been carried out. In this paper the results of ionic conduction and breakdown phenomena for anodic oxide films formed under galvanostatic conditions in the presence and absence of UV radiation are presented.

Materials and Methods

Specimens of area 2 cm² were cut, using a die from 0.25 mm thick sheet of 99.99% pure niobium (supplied by Aldrich). The method of the preparation of the specimens, chemical polishing procedure and the method of anodic oxidation was the same as that described previously[6]. A polished specimen was then placed in a glass cell, having a platinum wire gauge counter electrode and 0.1 N oxalic acid as the electrolyte. The cell was then placed in a UV chemical reactor (Shrinivasan-Griffin Rayonet type, manufactured by Gupta Scientific Industries, Ambala Cantt).

Anodic polarization of the specimen was carried out at constant current, adjusted through an electronically operated constant current generator (General Electronics, Ambala Cantt) designed specially for this purpose. The method of anodic polarization was same as described earlier[9]. The polarization under galvanostatic conditions were carried up to the breakdown voltage with AR grade oxalic acid electrolyte at different current densities and concentrations in the presence and absence of UV radiation. During the polarization the solution was stirred continuously with a magnetic stirrer. The anodic and cathodic reactions during the polarization were

(a) at anode [Nb → Nb⁺⁵ + 5e⁻] × 2

2Nb⁺⁵ + 10OH⁻ → Nb₂O₅ + 5H₂O

(b) at cathode 10H⁺ + 10e⁻ → 5H₂↑

The thickness of the oxide film was established using simple Faraday's law calculation. According to this the thickness (D in cm) of the film is calculated by D = MQ / 2zFAp (assuming z = 5, and 100% current efficiency for the film) where p is density of the oxide film, A is the total area of the film in cm², M is the molar mass of film material, z is the valency of the film, Q is amount of charge passed in coulombs and F is equal to 96488 coulombs. The density of Nb₂O₅ was taken to be 4.36 gm cm⁻³ as suggested by Holtzberg et al.[10]. The capacitance of the film in the dissolution experiments was measured using a capacitance bridge (Model CB 154-D/3, BPL, India). Each experiment was repeated at least five times and the breakdown voltage and dissolution data show a very good reproducibility.
Results and Discussion

Formation and dissolution rates of anodic oxide films in the presence and absence of UV radiation

Anodic polarization data are plotted in the form of formation voltage versus time of anodization in Fig. 1. The results presented in these linear plots are for films formed up to 125 V. However, a slight deviation from the linearity behaviour was observed beyond 125 V (not shown in Fig. 1). This indicates that the total current passing through the film does not remain totally ionic but part of it becomes electronic beyond 125 V. The rates of formation in the presence of UV radiation are found to be lower. This observation is contrary to the observations on the rate of formation of oxide films on other valve metals like Ta, Al, etc.

Nb$_2$O$_5$ films grown to 125 V in the presence and absence of UV radiation were dissolved in 24% HF solution. The data are plotted as reciprocal film capacitance versus time of dissolution of the film in Fig. 2. It is observed from Fig. 2 that the initial rate of dissolution is about three times faster for the film grown in the absence of UV radiation but it becomes very slow afterward. It seems that almost whole of the film has dissolved in few seconds, while film grown in UV radiation always has a slower rate of dissolution and it decreases further with time. This might indicate that the film grown in the presence of UV radiation is less porous (or more compact) and has a fewer flaw as compared to the film grown in the absence of UV radiation.

The slower formation and dissolution rate of Nb$_2$O$_5$ films in the presence of UV radiation can be explained by a model similar to that proposed by Vermilyea. During the formation of an anodic oxide film under high field, a positive space charge is created as a consequence of the excitation of valence electrons of the oxide into the
conduction band thus leaving positive holes in the oxide. As there would be a small barrier for the passage of electrons from the oxide, it would be difficult for electrons to jump from the solution to the full band of the oxide in order to fill the positive holes. As a result, a positive space charge near the oxide/solution interface would develop and the field at the interface would increase until the level of the holes in the full band decreases to the level of the electrons or ions in the solution (Fig. 3).

The fermi energy of Nb$_2$O$_5$ film is not known and hence an accurate estimate of the field required cannot be obtained. Initially, the thickness of film is very small, therefore, most of the radiation would be absorbed into the metal rather than into the oxide and little space charge would develop. Thus, the rate of formation of the film would be almost the same as that in the absence of UV radiation.

After the film had grown to a thickness of a few hundred Å, most of the light would be absorbed into the film, a positive space charge would develop and the field near the oxide solution interface would increase until the level of positive holes was equal to the level of electrons in the solution. To maintain the photocurrent, some electrons from the solution may jump directly to the oxide to neutralize the positive space charge at the interface. Thus the total current in the film would not remain ionic and part of it would become electronic. This would lead to the slower formation rate of the film. This has been observed experimentally for our system (Fig. 1).

As the electronic current in the film is increased the formation of the oxide would be smoother and its lattice would have fewer defects. Conversely, the film grown in the presence of UV radiation would be less porous than that grown in the absence of UV radiation. Thus the rate of dissolution of the less porous films would be slower as compared to the more porous film. This is also observed in our system (Fig. 2).

**Breakdown phenomena**

A number of voltages were proposed\textsuperscript{11} to define breakdown voltage. Breakdown voltage has been reported\textsuperscript{11} to be independent of current density, temperature, topography and method of pre-treatment of electrode surface. Further breakdown voltage has been found\textsuperscript{11-13} to be sensitive to the nature of anodized metal or composition and concentration of the electrolyte. In our earlier work we found that breakdown voltage depends upon concentration, current density, temperature and nature of electrolyte. In the case of niobium metal, breakdown is accompanied by the evolution of the oxygen gas at the surface. Under galvanostatic conditions, rate of gas evolution increases with time and voltage becomes static for sometime (say 100 s). This particular voltage is taken as breakdown voltage ($U_B$) for our investigations. The effect of UV radiation on the breakdown voltage was determined at various current densities ($j$ in A cm$^{-2}$) and range of resistivities ($\rho$ in Ω cm) in an oxalic acid solution. Figure 4 represents the variation of the breakdown voltage ($U_B$) with log $j$, while the plot of $U_B$ versus log $\rho$ are presented in Fig. 5 in the presence and absence of UV radiation. At the same current density $U_B$ is greater in the presence of UV radiation. However, the difference increases with the increase in the current density (Fig. 4). It can be observed from Fig. 5 that $U_B$ values in the presence of UV radiation are always higher than those in

![Fig. 3 - Schematic drawing of the electronic levels in the oxide film and on anions in the solution during the passage of photocurrent.](image)

![Fig. 4 - Plot of breakdown voltage versus log $j$.](image)
the absence of UV radiation for all resistivities of the solution.

According to Ikonopisov theory\(^\text{11}\) of breakdown voltage during anodization, the electrolytic contact not only provides ions for oxidation, but also injects electrons into the conduction band of the oxide. The high field strength can accelerate these electrons to an energy which is sufficient to free other (secondary) electrons by impact ionization, causing an avalanche multiplication to occur.

The avalanches effect cause the density \(j_e(x)\) of the electronics current to increase with distance \((x)\) within the anodic films according to

\[
j_e(x) = j_e(0) P\exp\left[\frac{eE}{\epsilon_m}(1/x + 1/x_r)\right]
\]

(1)

where \(j_e(0)\) is the primary current density injected at the electrolyte/oxide interface \((x = 0)\); \(e\) is the electronic charge; \(x_r\) is the recombination length; \(P\) is the probability for an electron to reach the unstable energy which is required for surmounting phonon scattering and \(\epsilon_m\) is the difference between the mean energy of an electron necessary for ionization and the mean energy of an electron emerging from an ionization event.

The general equation for the breakdown voltage is given by

\[
U_B = (\epsilon_m/e)\ln j_b - \ln j_e(0)
\]

(2)

where \(r = a_r/(a_r + 1) < 1\)
and \(x = a_rD\), where \(D\) is the thickness of the film and \(j_b\) is the electron current which is sufficient for the oxide destruction. The dependence of the breakdown voltage on the resistivity of the electrolyte can be expressed by the relation

\[
U_B = (\epsilon_m/e)\ln j_b - \ln j_e(0) - 2.3 b_r \log \rho
\]

(3)

where \(\rho\) is the resistivity of electrolyte. Parameters \(a_r\) and \(b_r\) are related to \(j_e(0)\) at constant temperature and field; for a particular metal and electrolyte

\[
j_e(0) = a_x \exp(-b_x)
\]

When the film is grown in the presence of UV radiation, a positive space charge develops at the interface and most of the electrons injected in the oxide are neutralized at the interface and thus the mean value of the recombination constant, \(r\), would decrease. At the same time, UV radiation also activates electrons in the oxide, and \(\epsilon_m\) increase in the presence of UV radiation. Therefore, from Eq. (3), \(U_B\) in the presence of UV radiation will be always higher at all resistivities as compared to \(U_B\) in the absence of UV radiation.

The primary electronic current density \(j_e(0)\) at the interface also depends on the concentration of anions in the solution. As the concentration of electrolyte decreases \((\log \rho\) increases\(\)), the number of electrons injected from the solution into the oxide will also decrease. This means that the recombination constant \((r)\) will increase with an increase of \(\log \rho\), and the difference between \(U_B\) values in the presence and absence of UV radiation will continue to decrease as has been observed in our system (Fig. 5).

Variation of \(U_B\) with current density \((j)\) or field strength \(E\) is given by

\[
U_B = (\epsilon_m/e)\ln j_b - \ln \alpha_x - \beta_x E^{1/2}
\]

(4)

where \(\alpha_x\) and \(\beta_x\) are constants and related through the relation

\[
j_e(0) = \alpha_x \exp(\beta_x E^{1/2})
\]

when temperature and resistivity of electrolyte are constant. According to Eq (4) \(U_B\) should decrease with increasing field \((E)\). This is in contradiction to the experimental observation for Ta, Al and Nb oxide films. \(U_B\) values are found to be independent of \(E\) for Ta and Al oxide films\(^{12-19}\) while these values increase with an increase of current density for Nb\(_2\)O\(_3\) films\(^9\). Ikonopisov\(^{11}\) has proposed that \(E\) has little effect on \(U_B\). This is because large variations in the current density only cause small changes, in the field. Thus \(U_B\) values

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_5.png}
\caption{Plot of breakdown voltage versus \(\log \rho\).}
\end{figure}
are found to be independent of the field. For Nb$_2$O$_5$ films, however, a hundred-fold increase in the current density causes an increase in $U_B$ of 120 V. The hundred-fold change of current density changes the field strength ($E^{1/2}$) only by 18% (ref. 9). Therefore, either $U_B$ is very sensitive to applied field or some other constant ($\epsilon_m$ or r) also changes simultaneously with E. By definition, $\epsilon_m$ is the difference between the mean energy of an electron necessary for ionization and the mean energy of electron emerging from an ionization event. As the value of E increases, the mean energy of electron emerging from an ionization event will also increase. Thus, $\epsilon_m$ will also increase. The $U_B$ should increase with an increase of E.

When the film is irradiated with UV radiation, the electrons in the oxide would be excited and the difference between the mean energy of an electron jumping from solution to oxide and the mean energy of the electron emerging from the ionization event would increase, or $\epsilon_m$ would increase. Thus $U_B$ values at particular values of E would be increased in the presence of UV radiation as compared to those in the absence of radiation. When the field is increased in the presence of UV radiation the value of $\epsilon_m$ also increases further, and differences between $U_B$ values in the presence and the absence of UV radiation also increase with an increase of the field. In fact, this has been observed experimentally (Fig. 3 and Fig. 6). Since the electronic current during formation of films in the presence of UV radiation increases, the thickness of the film and the value of E cannot be estimated by the Faraday’s law method. The magnitudes of field (E) in the presence of UV radiation at a particular current density are taken to the same as in the absence of UV radiation. The calculation of the field in the absence of UV radiation was made by the usual Faraday’s law method, when the electronic current is negligible. This has been described earlier.

It can be concluded that, in the presence of UV radiation, the reduced rate of formation of anodic Nb$_2$O$_5$ films is due to the development of a positive space charge near the solution/oxide interface. Increase in the breakdown voltage value in the presence of UV radiation may be due to a decrease in the recombination constant (r) and/or increase in the impact ionization constant ($\epsilon_m$).

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References