

Electrochemical Formation and Properties of n-GaAs / Au and n-GaAs / Ag Schottky Barriers.

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Semiconductor / metal Schottky barriers are important in integrated circuit technology as well as for light detection and solar energy conversion purposes. Electrochemical metal deposition constitutes an elegant way to prepare such barriers. In the present contribution, the electrochemical formation of n-GaAs / Au and n-GaAs / Ag Schottky barriers is studied and their properties are correlated to the electrochemistry of the systems under investigation and compared to those of the vacuum-deposited analogues.

The electrochemical measurements were made on (100)GaAs electrodes in aqueous 5 mM complexed Au(I) (pH=14) or Ag(I) (pH=2.7, 8 and 14) solutions. Gold or silver layers were electrodeposited on n-GaAs by instantaneously switching the electrode potential from open-circuit potential V_{oc} to a given deposition potential V_D , and electrodeposition was stopped by switching back to V_{oc} . As all reduction reactions involved were found to be conduction band processes, metal deposition only occurs at V_D , which allows to determine the amount of metal formed and hence the average metal layer thickness d coulometrically. Interfaces with good adhesion properties and good Schottky barrier characteristics were obtained. In what follows, the focus will be on the barrier height Φ_B .

Electrodeposition of Au layers with $d = 150$ nm was performed at various values of V_D . Going from less to more negative V_D values, a transition in Φ_B was observed from a higher value $\Phi_{B,h}$ to a value $\Phi_{B,l}$ which is about 0.06 eV lower, the transition deposition potential $V_{D,tr}$ being around -1.67 V vs. SCE. For 75 nm Au layers, the same transition was observed, but at more negative V_D , Φ_B rises again. For $d = 25$ nm and $d = 12$ nm, the barrier height was $\Phi_{B,h}$ at all V_D .

Gold layers with $d = 12$ nm were also deposited on n-GaAs by evaporation from a vacuum. The height of the barriers formed that way was systematically lower than that for 12 nm layers deposited electrochemically. After annealing both barrier types in an inert atmosphere for 10 min. at 150°C , the height of the barriers made by evaporation remained unchanged, whereas the height of the barriers prepared electrochemically decreased to the values observed for the former.

From IR measurements it has been concluded that in the potential range corresponding to the present electrodeposition experiments, the As surface lattice sites are hydrogen-terminated whereas the Ga sites are not⁽¹⁾. It is reasonable to assume that the latter are covered, at pH=14, by $-\text{O}^-$ ions. As below $V \cong -1.6\text{V}$ vs. SCE at pH=14, a thermodynamically stable Ga phase can be formed on the GaAs surface, the $-\text{O}^-$ ions will detach from the surface below $V \cong -1.6\text{V}$ vs. SCE at pH=14, i.e. approximately at the observed $V_{D,tr}$ value. We assume that, when Au is electrodeposited at a GaAs surface containing $-\text{O}^-$ groups, a $\text{Au}^{\delta+} - \text{O}^{\delta-}$ dipole layer forms at the GaAs / Au interface, leading to an additional contribution to the interfacial barrier height. This hence explains the results for $d = 150$ nm. For understanding the results for thinner gold layers (25 nm and 12 nm) deposited electrochemically, it is important to realize that these layers are porous⁽²⁾, so that when switching back to V_{oc} after electrodeposition, water penetrating through these thin layers may reoxidize the interface, thus enhancing the barrier. This may explain why here, $\Phi_{B,h}$ is observed in the entire V_D range. The case of intermediate Au layer thickness ($d = 75$ nm) can be understood by observing that at the most negative V_D values, H_2 evolution may lead to an increased porosity of the layer. The difference between barriers formed by "wet" and by "dry" procedures is then obvious from the fact that in the latter case, no $-\text{O}^-$ groups are present on the surface. The effect of annealing of the barriers formed electrochemically can be ascribed to thermal decomposition of the interfacial oxides.

Further support for this interpretation is obtained from results on 150 nm Ag / GaAs Schottky barriers, which show the same features as their Au counterparts, with the same value of $V_{D,tr}$ at pH=14, and with a pH-change of this quantity

over -0.06 V per unit pH increase; the latter effect can be rationalized from the pH-dependence of the GaAs to Ga + AsH_3 reduction reaction.

References

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