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Photoelectrochemically-Induced Gold Deposition on p-GaAs Electrodes

Part I. Nucleation and Growth

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ABSTRACT

This paper reports on the deposition of Au on cathodically biased p-GaAs electrodes from alkaline KAu(CN)₂ solutions in the dark or under illumination. Nucleation and growth of Au have been studied by potentiodynamic and potentiostatic current measurements in combination with scanning and transmission electron microscopy. Au deposition is char-acterized by progressive nucleation and three-dimensional growth followed by coalescence of Au particles. Different mechanisms of electron transfer processes occurring during nucleation and growth are discussed. Au nucleation in the dark occurs readily at relatively high-doped ($>5 \times 10^{17}$ /cm³) electrodes, both in the absence and presence of excess CN⁻ ions. Selective photoinduced nucleation is possible on low-doped ($<2 \times 10^{17}$ /cm³) electrodes in a solution with excess CN⁻ ions. It is observed that the critical size of Au nuclei is smaller than 1 nm. Growth of previously formed Au nuclei can proceed in the dark and is initially controlled both by kinetic factors and diffusion of $Au(CN)_2^-$ ions. Our results indicate that only a small potential barrier exists between p-GaAs and deposited Au particles.

Photoselective metal deposition on semiconductors attracts much attention for potential application in the fabrication of microelectronic circuits and devices and imaging systems. A focused laser beam or mask projection was previously used to produce localized metal plating from solutions on semiconductor substrates such as TiO₂ (1), GaAs (2-6), Si (4-8), and InP (2, 9-11). Recently, we reported that photocathodic deposition of gold alloys can be used to make local ohmic contacts to p-type III-V materials (2).

Localized illumination of a semiconductor in a solution which contains metal ions may result in the deposition of spatially resolved metal patterns (positive photoimaging) if photogenerated electrons in the semiconductor can reach the surface. Recombination and (lateral) diffusion of photoelectrons at the semiconductor surface must therefore be minimized (6). For a p-type electrode at open circuit, the downward bending of the energy bands at the surface is usually so small that cathodic photocurrents are inhibited by strong recombination via surface states or an efficient back reaction via the valence band (12, 13). Negative biasing increases the downward band bending so that photogenerated electrons and holes are effectively separated by the space charge field. The electrons are drawn to the surface while the holes are swept into the bulk and out through the external circuit.

With a view to making more efficient practical use of laser beams for metal patterning, it seemed worthwhile to study the possibility of electroless deposition (14) or electrodeposition of metal on previously photodeposited metal clusters on semiconductor substrates. In the present two papers we describe a study of various aspects of photoelectrochemically induced Au deposition on p-GaAs electrodes. The solutions used are derived from an alkaline electroless gold cyanide solution which contains KBH4 as a reducing agent (15). This paper (Part I) describes nucleation and growth of Au, studied by electrochemical techniques and electron microscopy. Au was deposited uniformly on relatively large p-GaAs surfaces in solutions without KBH₄, both in the dark and under illumination. Part II deals with various size effects revealed in experiments in which the electrode was locally illuminated (16). These include the possibility of electroless Au deposition on small photoelectrochemically deposited Au spots. A separate study on the reduction of dissolved oxygen at p-GaAs electrodes has been published elsewhere (17). This reaction may compete with the reduction of Au ions and plays an important role in the experiments described in Part II.

Experimental

Three different aqueous alkaline solutions were used (15). They contained 0.2M KOH and additionally the components $5 \times 10^{-3}M$ KAu(CN)₂ and/or 0.1M KCN; they are denoted as such by KAu(CN)₂, KCN, and KAu(CN)₂/KCN. All solutions were prepared with triply distilled water and reagent-grade chemicals obtained from Merck. All experiments were carried out at room temperature. Unless otherwise stated, no gas was bubbled through the solution.

Zinc-doped p-type GaAs single-crystal wafers with (100) orientation and a carrier density (N_A) in the range $9 imes 10^{16}$ - 2×10^{19} /cm³ were obtained from MCP Electronics. Ohmic contacts on the back side were made by Zn diffusion and high vacuum evaporation of Pt, Ta, Pt, and Au through a mask plate. The contacts were subsequently annealed in Ar gas at 410°C for 15 min. Electrodes were mounted in a Perspex holder as shown in Fig. 1a. A copper wire was fixed to the ohmic contact by a conducting resin (E-Solder No. 3021 from ACME). An adhesive tape (Macal 8100-series) with a circular hole (3 mm diam) covered the front of the electrode. Prior to use, the electrodes were etched in a H₂O/H₂O₂(30%)/NH₄OH(25%) (volume ratio 100:2:1) solution and dipped in a 0.2M KOH solution. Deposited Au was removed by dipping the electrode in Imastrip-Au solution (Imasa B.V., The Netherlands) at 60°C for 1 min. A p-GaAs electrode on which Au was deposited is denoted as GaAs(Au).

Specimens for scanning and transmission electron microscopy (SEM and TEM, respectively) were in the form of electrodes, which permitted a direct correlation between electron microscopy observations and electrochemical

measurements. During the preparation of these specimens the solutions were purged of oxygen in order to minimize dissolution of Au after deposition (16). The solution was therefore saturated with N_2 and experiments were carried out in N_2 atmosphere. Also, the time which a specimen spent in solution was minimized. After Au deposition the electrodes were carefully rinsed in N_2 -saturated water and subsequently dried quickly in flowing N_2 gas.

Electrodes as described above could be investigated directly by SEM. A subsequent evaporation of a thin metal film to prevent charging of the specimen during electron beam irradiation was not necessary. Specimens for TEM were prepared in the following way (Fig. 1b). A rectangular piece ($\approx 3 \times 6 \text{ mm}^2$) of a p-GaAs wafer with an ohmic contact on a part of the back side was placed on a rotating holder. A circular hole was etched in the wafer by a small stream of a Cl₂/CH₃OH solution which was directed to the back side. Etching was stopped as soon as incident light on the front side was transmitted through the hole. The wedge-shaped edges of the hole then contained areas which were sufficiently thin (i.e., electron transparent) to be suitable for TEM investigations. After making electrical contact and insulating with beeswax, the wafer was used as an electrode on the front of which Au was photoelectrochemically deposited. TEM specimens ($\approx 3 \times 3 \text{ mm}^2$) were subsequently obtained by cutting the electrode in half. SEM and TEM investigations were carried out with a Philips SEM505 (operated at 30 kV) and a Philips EM400T (operated at 120 kV) electron microscope, respectively.

Potentiodynamic, potentiostatic, and open-circuit measurements were made in a conventional electrochemical cell using a large Pt counterelectrode and a saturated calomel electrode (SCE) as reference. All potentials are quoted with respect to SCE. The external bias was applied by an EG&G PAR Model 175 universal programmer in combination with an EG&G PAR Model 173 potentiostat/galvanostat. The current signals during current-potential and current transient measurements were detected by a Philips PM 8141 X-Y recorder and a PAR Model 4101 scan recorder, respectively.

Uniform illumination of the electrode surface was carried out with an expanded beam of a Spectra Physics HeNe laser ($\lambda = 632.8 \text{ nm}$) or Ar⁺ laser ($\lambda = 454.5-514.5 \text{ nm}$). In some experiments the laser beam was modulated by using a Uniblitz Model 310 B shutter-time control with a rise time of 0.4 ms. The light intensity was attenuated by using neutral density filters (Spindler & Hoyer) or glass filters (Saale, BG 23). Light intensities were measured by a photovoltaic detector (EG&G Model 460 laser power meter) and were in the range 0.5-500 mW/cm².

Results

Electrodeposition in the dark.—Figure 2 compares current-potential curves of a p-GaAs electrode with a high carrier density $(1.5 \times 10^{19}/\text{cm}^3)$ in the KAu(CN)₂ solution (Fig. 2a) and in the KAu(CN)₂/KCN solution (Fig. 2b) in the dark. During the first cathodic scan in the KAu(CN)₂ solution, a diffusion-controlled (see below) cathodic peak due to reduction of gold ions is observed around -1.05V (solid curve in Fig. 2a). The strong current increase at more ca-



Fig. 1. Cross-sectional side view of (a) electrode holder and (b) TEM specimen electrode.



Fig. 2. Current-potential curves for p-GaAs electrodes $(1.5 \times 10^{19}/ \text{ cm}^3)$ in the dark. (a) KAu(CN)₂ solution. (b) KAu(CN)₂/KCN solution. Sweeps were made starting at -0.5V in negative direction. Scan rate 10 mV/s. The solid curves refer to the first sweep. The dashed curves refer to the second (a) and fourth sweep (b), respectively.

thodic potentials is due to H_2 formation on previously deposited Au. In the subsequent anodic scan no dissolution of Au occurs since the reversible redox potential $V(Au(CN)_2^-/Au)$ is very positive (+0.60 V) due to the low concentration of CN^- ions. In the second sweep (dashed curve in Fig. 2a) the diffusion-controlled cathodic peak is less pronounced.

In the KAu(CN)₂/KCN solution electrodeposition of Au in the dark starts only at -1.25V (solid curve in Fig. 2b). The low background current is due to reduction of dissolved oxygen (17). Au dissolution occurs at potentials more positive than V(Au(CN)₂⁻/Au) which equals $\approx -0.89V$ in this solution (18). At more negative potentials, the cathodic current increases with the number of scans. After four scans the recorded current-potential curves (dashed curve in Fig. 2b) did not change. The dashed curves of a bulk Au electrode in these solutions. In particular, the zero-current potential of a GaAs(Au) and a Au electrode in the KAu(CN)₂/KCN solution are the same.

It is noted that afer a few hours under open-circuit conditions in the dark, a discontinuous Au film was deposited on p-GaAs electrodes in the KAu(CN)₂ solution, but not in the KAu(CN)₂/KCN solution. This deposition is due to electroless exchange between gold ions and the p-GaAs surface, which is favored when V(Au(CN)₂⁻/Au) is more positive than the flatband potential ($V_{\rm FB}$) of the electrode. At $pH \approx 13.3$, $V_{\rm FB}$ is estimated to be $\approx -0.4V$ (19).

Figure 3 shows current-potential curves of three p-GaAs electrodes with different carrier densities in the KCN solution (curves a-c) and in the KAu(CN)₂/KCN solution (curves d-f) in the dark. In the KCN solution the electrodes show rectifying behavior in a wide range of negative potentials. In the KAu(CN)₂/KCN solution, however, the onset of gold ion reduction is shifted toward cathodic potentials with decreasing carrier density. Obviously, Au electrodeposition in the dark is suppressed at lower doping levels. This was also observed in the KAu(CN)₂ solution, but here a gradual increase in the rate of gold ion reduction occurred, even at the lowest doping level $(10^{17}/cm^3)$.



Fig. 3. Current-potential curves for p-GaAs electrodes in the KCN solution (curves a-c) and in the KAu(CN)₂/KCN solution (curves d-f) in the dark. N_A was: 1.8×10^{17} /cm³ (curves a and d), 1.8×10^{18} /cm³ (curves b and e), and 1.5×10^{19} /cm³ (curves c and f). One cathodic scan was made starting at -0.6V. Scan rate 10 mV/s.

Au electrodeposition from the KAu(CN)₂/KCN solution in the dark is further illustrated by potentiostatic measurements and SEM observations. Figure 4a shows current transients at -1.7V for three p-GaAs electrodes with different doping levels. Figure 4b shows current transients at different cathodic potentials and a fixed doping level $(1.8 \times 10^{18}/\text{cm}^3)$. A part of the cathodic current at negative potentials (<-1.5V) is due to H₂ formation on electrodeposited Au. The occurrence of a characteristic current



Fig. 4. Potentiostatic current-time transients for p-GaAs electrodes in the KAu(CN)₂/KCN solution in the dark. At t = 0 the potential was stepped from $V_{\infty} = -0.67V$ to the potential indicated. (a) Deposition potential -1.7V. N_A was varied: 1.8×10^{17} /cm³ (curve a), 1.8×10^{18} / cm³ (curve b), and 1.8×10^{19} /cm³ (curve c). (b) N_A = 1.8×10^{18} /cm³. The deposition potential was varied. maximum (at $t = t_m$) indicates a diffusion-controlled growth of previously formed Au particles (20-22). At increasing doping levels (Fig. 4a) or increasing negative potentials (Fig. 4b), the current maximum moves toward shorter times and higher currents, indicating higher nucleation rates. This was confirmed by SEM observations of the electrode after Au deposition. The density of the observed Au particles (>10 nm) increased when either the doping level, the overpotential, or the deposition time was increased. The increase of the density at longer times is due to progressive nucleation. Nuclei densities were in the range 108-1010/cm². At deposition times much longer than $t_{\rm m}$ in the corresponding current transient, the growing Au particles coalesced to form a porous network. As an example, Fig. 5 shows SEM images of an Au film electrodeposited on a high-doped $(2.0 \times 10^{19}/\text{cm}^3)$ p-GaAs electrode at -1.4V in the KAu(CN)₂/KCN solution. Under these conditions, a current maximum was observed at $t_{\rm m}$ = 3.5s. At 5s the deposited Au film consists of three-dimensional Au particles in the 25-250 nm size range with a density of $\approx 3 \times 10^{9}$ /cm² (Fig. 5a). A relatively thick Au film with a porous structure is deposited after 80s (Fig. 5b). Au electrodeposition was more pronounced at scratches and other surface defects.

Photoinduced electrodeposition.—From the above results it follows that Au electrodeposition at negative potentials in the dark is not initiated on low-doped ($<10^{17}$ / cm³) p-GaAs electrodes in the KAu(CN)₂/KCN solution. However, it was shown previously that under these conditions selective electrodeposition of Au patterns in the dark can be initiated by selective illumination (2). Our further experiments are restricted to this photoinduced Au elec-



Fig. 5. SEM images of p-GaAs electrodes (2.0×10^{19} /cm³) onto which Au was potentiostatically deposited from the KAu(CN)₂/KCN solution (N₂ saturated) in the dark at -1.4V for 5s (a) and 80s (b).



Fig. 6. Current-potential curves for illuminated p-GaAs electrode (1.8 \times 10¹⁷/cm³) in the KAu(CN)₂/KCN solution. Two sweeps were made starting at V_{oc} (indicated) in negative direction. The solid and dashed curves refer to the first and second sweep, respectively. Scan rate 10 mV/s. Light intensity 38 mW/cm².

trodeposition on uniformly illuminated low-doped electrodes in the $KAu(CN)_2/KCN$ solution.

Figure 6 shows current-potential curves for an illuminated electrode. In the first cathodic scan a diffusion-controlled cathodic peak due to reduction of gold ions appears around -1.15V (solid curve). The background cathodic current is due to diffusion-controlled O₂ photoreduction (17). H₂ evolution starts already at -1.3V. In the anodic scan Au dissolution starts at potentials anodic of -0.87V. In subsequent sweeps illumination did not significantly affect the (dashed) curves which were very similar to those of a bulk Au electrode.

Figure 7 shows an example of a set of current transients for an illuminated electrode at different potentials. The inset shows the initial currents on a shorter time scale. A sharp current peak occurs immediately after the start of illumination at t = 0. This peak is due to mass-transportcontrolled O₂ photoreduction (17). The current maximum after this peak again indicates a diffusion-controlled growth of previously formed Au particles. A plot of the decreasing current after the maximum at -1.2V vs. the inverse square root of time (Cottrell plot) gave a straight line indicating linear diffusion of Au(CN)2⁻ ions to a planar electrode. From the slope a diffusion coefficient $D \approx 1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ was obtained for the Au(CN)₂⁻ ions. When either the overpotential (see Fig. 7) or the light intensity (not shown) was increased, the O2 reduction peak became sharper and the current maximum moved toward shorter times and higher currents. The latter corresponds



Fig. 7. Potentiostatic current-time transients for illuminated p-GaAs electrode (1.8×10^{17} /cm³) in the KAu(CN)₂/KCN solution. At t = 0 the potential was stepped from $V_{oc} = -0.67V$ to the potential indicated, and the light was switched on. Light intensity was 38 mW/cm². The inset shows the initial cathodic current on a shorter time scale.

again to a higher Au nucleation rate, as was confirmed by electron microscopy observations.

The nuclei densities observed with SEM or TEM were in the range 5×10^9 - 5×10^{12} /cm². Nearly continuous Au films were observed at relatively large nucleation rates and long illumination times. It should be noted that TEM observations on thin p-GaAs electrodes correlated with SEM observations on bulk p-GaAs electrodes (the nucleation behavior of Au on the thin electrodes could have been different from that of bulk electrodes, since locally the thickness of the TEM specimen is similar to the thickness of the space charge layer in bulk electrodes).

Figure 8 shows a SEM image of the Au film deposited during illumination (38 mW/cm²) for 4s at -1.1V, which corresponds with point A in the current transient shown in Fig. 7. The Au film consists of spherical Au particles in the 10-50 nm size range with a density of $\approx 2 \times 10^{10}$ /cm². Note that coalescence of Au particles has not taken place, although the deposition current already passed through a maximum at $\approx 0.6s$ (Fig. 7).

Particularly at nuclei densities larger than 5×10^{10} /cm², it was necessary to use TEM, since in these cases individual growing particles could not be resolved by SEM before they coalesced. Figure 10 shows TEM images of four subsequent stages of Au deposition under illumination (0.68 mW/cm^2) at -1.2V, corresponding to the times a, b, c, and d in the current transient shown in Fig. 9. After t = 0.4s, Au particles in the 1.0-3.5 nm size range with a density of $\approx 5 \times 10^{11}$ /cm² were visible (Fig. 10a). In a similar experiment without illumination, no particles were observed. Dark field imaging showed that the particles were crystalline and randomly oriented on the GaAs substrate. The observation that 1 nm Au nuclei are stable implies that the critical nucleus size is smaller than 1 nm (23). Au nuclei larger than this critical size tend to grow, since this decreases their Gibbs free energy. At t = 0.8s, *i.e.*, before the current maximum, the size range of the Au particles was enlarged to 1.0-7.0 nm and the density was increased to $\approx 8 \times 10^{11}$ /cm² (Fig. 10b). The larger Au particles (>3 nm) showed the characteristic diffraction contrasts due to (multiple) twinning. Coalescence of growing crystallites was observed at t = 2.0s (Fig. 10c). Note the droplet-like morphology of the largest agglomerates and the frequent occurrence of neck formation. At t = 8.0s, a complex polycrystalline Au network was observed (Fig. 10d).

Finally, it will be shown that after previous illumination, Au electrodeposition can proceed in the dark. The transi-



Fig. 8. SEM image of a p-GaAs electrode $(1.8 \times 10^{17}/\text{cm}^3)$ onto which Au was photoelectrochemically deposited from the KAu(CN)₂/KCN solution (N₂-saturated) by illumination for 4s at -1.1V. Light intensity 38 mW/cm² (cf. point A in Fig. 7).

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Fig. 9. Potentiostatic current-time transient for illuminated p-GaAs electrode ($1.8 \times 10^{17}/\text{cm}^3$) in the KAu(CN)₂/KCN solution (N₂-saturated). At t = 0 the potential was stepped from V_{oc} = -0.67 to -1.2V and the light was switched on. Light intensity 0.68 mW/cm².

tion from light-sensitive to dark reduction of gold ions was investigated by measuring current transients after a light pulse of variable length (Δt). Figure 11 shows the results of two of these experiments: one at a low light intensity (1.9 mW/cm², Fig. 11a) and the other at a high light intensity (500 mW/cm², Fig. 11b) so that mass transport of gold ions was already limited by linear diffusion at $\Delta t \approx 50$ ms. The initial current recorded under continuous illumination follows curve f. When the light was switched off at $t = \Delta t$, the current dropped immediately and gained (after a short anodic spike) a value given by the dashed curve. Curves a-e show the currents recorded in the dark after various illumination times (Δt). The dashed curve represents the recorded dark current when the light was interrupted continuously for a very short time (<10 ms). As is shown, the dark currents increased considerably when Δt was increased. They are due to gold ion reduction, since in control experiments these GaAs(Au) electrodes showed negligible dark currents at -1.2V in the KCN solution.

From Fig. 11 it is clear that the total current due to photocathodic Au deposition (curve f) consists of a dark current, represented by the dashed curve, and a photocurrent given by the difference between curve f and the dashed curve. The contribution of the photocurrent, and consequently the quantum efficiency for gold ion reduction, is initially relatively large but decreases rapidly with increasing deposition time. From Fig. 11 it is roughly calculated that the maximal quantum efficiency in the initial stages of illumination decreases from 0.7 to 0.04 when the light intensity increases from 1.9 mW/cm^2 to 500 mW/cm². This can be attributed to an enhanced rate of surface recombination (12) and a more rapid control of the reduction reactions by mass transport.

Discussion

On the basis of the above results, we will discuss possible mechanisms for the electron transfer from p-GaAs to gold ions during nucleation and growth, respectively. After this, the current transients and electron microscopy observations are discussed. It should be noted that nucleation refers to the formation of a Au nucleus with a critical size (23) smaller than 1 nm (Fig. 10a), whereas growth refers to the expansion of the critical nucleus. Figure 12 shows the energy levels of the p-GaAs electrode and of relevant redox couples (18) in the solution ($pH \approx 13.3$).

Electron transfer during nucleation.—The CN^- ion is a very strong complexing agent for Au^+ ions (18). Hence, the main difference between the $KAu(CN)_2$ and the $KAu(CN)_2/$ KCN solution is that in the latter solution the concentration of Au^+ ions is drastically reduced due to the excess CN^- ions. The concentration of $Au(CN)_2^-$ ions is nearly equal in both solutions. From a comparison of the initial dark currents of electrodes in these solutions (e.g., Fig. 2), it is suggested that the dark current in the $KAu(CN)_2$ solution is initiated by nucleation of Au due to reduction of uncomplexed Au^+ ions. This might occur for both high- and low-doped electrodes in the $KAu(CN)_2$ solution. The Au^+/Au redox potential corresponds to the valence band of p-GaAs, so that Au^+ ions can be reduced by hole injection in the dark.

In the KAu(CN)₂/KCN solution the concentration of Au⁺ ions is so low that Au deposition most probably occurs via reduction of complexed gold ions. The electroactive species in Au(CN)₂⁻ reduction is AuCN, which is in chemical equilibrium with Au(CN)₂⁻ ions (24, 25). The redox potential of the AuCN/Au couple corresponds to V(Au(CN)₂^{-/} Au) (25) and is situated well above the valence bandedge of p-GaAs. The dark currents found with relatively highdoped electrodes in the KAu(CN)₂/KCN solution (Fig. 2b, 3, and 4) may therefore be initiated by the formation of Au nuclei due to tunneling of electrons from valence band states to AuCN species (say Au(CN)₂⁻ ions). The probability of tunneling increases with increasing doping level (N_A),



Fig. 10. TEM bright field images of Au deposit on p-GaAs electrode, corresponding to times a (t = 0.4s), b (t = 0.8s), c (t = 2.0s), and d (t = 8.0s) denoted in Fig. 9.

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Fig. 11. Potentiostatic current-time transients for p-GaAs electrodes $(9 \times 10^{16}/\text{cm}^3)$ in the KAu(CN)₂/KCN solution in the dark after a light pulse of variable length (Δt) . At t = 0 the potential was stepped from $V_{oc} = -0.67$ to -1.2V and the light was switched on. From t = 0 the current under illumination follows curve f. At $t = \Delta t$ the light was switched off, but the potential remained at -1.2V. The current then dropped immediately and gained (after a short anodic spike) a value given by the dotted curve. From $t = \Delta t$ the dark current follows one of the curves a-e. The dashed curve represents the recorded dark current time (<10 ms). (a) Light intensity 1.9 mW/cm²; Δt is 50, 100, 200, 500, 1000, and 5000 ms for curves a-f. (b) Light intensity 500 mW/cm²; Δt is 10, 20, 50, 100, 200, and 1000 ms for curves a-f.

since the space charge layer thickness is proportional to $N_A^{-1/2}$ (26). Alternatively, one can ascribe the initial formation of Au nuclei to the reduction of Au(CN)₂⁻ ions by thermally generated conduction band electrons in the space charge layer. In general, the latter are responsible for a blocking (leakage) current which increases with increasing doping level (27).

Reduction of Au(CN)₂⁻ ions at low-doped electrodes in the KAu(CN)₂/KCN solution occurs only under illumination at potentials cathodic of -1.0V (Fig. 3, 4a, 6, and 7). Since the empty states of the Au(CN)2-/Au couple are located mainly between the valence band and the conduction band (Fig. 12), we assume that, in accordance with a model proposed by Kelly and Memming (12), photogenerated electrons are transferred to the solution via surface states within the bandgap. Formation of Au nuclei with a critical size starts only when a critical concentration of electrons is built up at the surface, *i.e.*, when sufficient electrons are trapped in surface states. Assuming that $V_{\rm FB} \approx -0.4 {
m V}$ at $p{
m H} \approx 13.3$ (19), this requires a negative energy band bending of 0.6V or more. Only then is recombination sufficiently reduced due to the low concentration of holes at the surface.

Electron transfer during growth.—The deposition of a small amount of Au drastically changes the potential distribution at the semiconductor-electrolyte interface, as was indicated by our recent impedance measurements (2). When a relatively large amount of Au (say 10 nm thickness) is deposited, the current-potential behavior of the GaAs(Au) electrode in the dark is similar to that of a bulk Au electrode (Fig. 2 and 6). From these results three important conclusions can be drawn. Firstly, in the studied potential range the Fermi levels (E_F) of p-GaAs and Au are equal in the dark. Secondly, changes in the applied poten-



Fig. 12. Energy diagram showing the bandedges (E_c , E_v) of p-GaAs at pH = 13.3 with respect to redox levels relevant to the present work.

tial appear across the Helmholtz double layer at the metalelectrolyte interface. This means that the Fermi level in the semiconductor is pinned at the semiconductor-metal interface. It has been suggested that Fermi level pinning is due to induced formation of semiconductor defects at the interface during the initial stages of metal deposition (28), but other models have also been proposed (29). The third conclusion which follows from the ohmic current-potential behavior of a GaAs(Au) electrode is that the Schottky barrier height (ϕ_B) at the p-GaAs/Au junction must be small. This was also found by Reineke and Memming who suggested that the barrier height of electrochemically formed p-GaAs/metal contacts must be smaller than 0.3V (30).

Following the concepts of Nakato *et al.* (31, 32), Fig. 13 shows schematic energy band diagrams for a part of a cathodically biased p-GaAs electrode covered with a Au particle of: (a) small size (<3 nm), (b) medium size (10-25 nm), and (c) large size (>50 nm). The band bendings in the space charge layer of the semiconductor in the bare and metal-covered parts are represented by solid and dashed lines, respectively. The conduction bandedge $E_c(M)$ and the valence bandedge $E_v(M)$ at the p-GaAs/metal interface should shift with a change in the applied potential, since it is assumed that the barrier height ϕ_B has a small constant value. The bandedges $E_c(S)$ at the



Fig. 13. Schematic energy band diagrams for a part of a cathodically biased p-GaAs electrode covered with a Au particle of (a) small size (<3 nm), (b) medium size (10-25 nm), and (c) large size (>50 nm). The band bendings in the space charge layer of p-GaAs at the bare and gold-covered parts are denoted by solid and dashed lines, respectively. Charge transfer processes in the dark and under illumination are represented by arrows in (c) and (a), respectively. bare p-GaAs parts remain constant at levels determined by the adsorption of ions such as OH⁻. Therefore, the energy bandedges change rather sharply at the boundary between metal-covered and bare p-GaAs parts (32). An important point is that the band modulation caused by a small Au particle (dashed lines in Fig. 12a) diminishes very rapidly toward the interior of the semiconductor and becomes negligibly small at distances comparable with the size of the Au particle (32). On the contrary, for a large Au particle, the band modulation extends deep into the space charge layer of the semiconductor, as shown in Fig. 12c (for a doping level of $10^{17}/\text{cm}^3$ the thickness of the space charge layer is of the order of 100 nm).

The behavior of p-GaAs electrodes coated with a discontinuous Au film lies between that of a bulk Au electrode and that of a bare p-GaAs electrode (31, 32). The actual behavior is determined by the size of the Au particles and the gap areas between them, since, for a given value of ϕ_B , these two parameters determine the band modulation inside the space charge layer of the semiconductor. When the distance between Au particles approaches the size of the Au particles, the band modulation will be smoothed out in the space charge layer.

Figure 13 can now be used to explain the characteristic features of Au deposition, namely, three-dimensional growth and progressive nucleation, which are observed both in the dark and under illumination.

Three-dimensional growth.—A newly formed Au nucleus represents a metal microelectrode with a potential determined by the Fermi level in the semiconductor. Consequently, a Au nucleus behaves as a microcathode at which electrons can be transferred to Au(CN)2⁻ ions, leading to three-dimensional growth (Fig. 5, 8, and 10). It should be noted that this mechanism of charge transfer is independent of that during nucleation (see the previous section). Nucleation has an accelerating effect on the Au deposition current that is almost completely due to the growth of existing Au particles (the current due to nucleation is extremely small). Growth occurs only when two conditions are fulfilled. Firstly, the applied potential must be sufficiently negative with respect to $V_{\rm FB}$ in order to drive electrons from the semiconductor to the Au nuclei. Secondly, the potential of the Au nuclei must be cathodic of the redox potential V(Au(CN)2^{-/}Au) (see e.g., Fig. 2).

Under illumination photoexcited electrons in the conduction band are driven to the surface and tunnel through a potential barrier into the Au particles. From Fig. 13 it is expected that this should occur more easily for smaller Au particles since the width of this barrier increases with increasing size of the Au particle. In the dark, valence band electrons at the metal-covered surface must overcome the Schottky barrier to enter the Au particles. Figure 13 shows that for small Au particles, the availability of valence band electrons is relatively low and that the effective barrier height is larger than ϕ_{B} . It is therefore expected that growth by electrodeposition in the dark is most favorable for larger Au particles. This agrees with the observations of Nakato et al. (33) that p-type semiconductor electrodes covered with a discontinuous metal film (i.e., small metal particles) show small cathodic dark currents due to H₂ evolution, whereas these electrodes exhibit ohmic behavior when they are covered with a nearly continuous metal film (i.e., extremely large metal particles).

Progressive nucleation.—From Fig. 13 it also follows that during growth of existing Au nuclei, new Au nuclei can still be formed according to one of the mechanisms described in the previous section. The principal reason for this is that the semiconductor surface energy levels at bare p-GaAs parts are not noticeably affected by the presence of neighboring Au particles. However, it is expected that the rate of nucleation depends on the growth of existing particles, since this affects the availability of both Au ions and electrons at bare p-GaAs surface sites.

Analysis of current transients and electron microscopy observations.—Growth determined both by kinetics and diffusion.—According to the usual description of threedimensional multiple nucleation with diffusion-controlled growth (20, 21), the characteristic shape of the current transients for the initial stages of Au deposition (Fig. 4, 7, 9, and 11) can be explained as follows. The rising part is due to the increase in electroactive surface area as each Au nucleus grows, and the number of Au nuclei increases due to progressive nucleation. During this stage the diffusion zones around the nuclei should expand until they overlap. This should cause the current maximum at time t_m , after which the fall in current reflects linear diffusion of Au(CN)₂⁻ ions to an effectively planar electrode.

From a correlation between current transients and electron microscopically observed nuclei densities, it could be established that growth of individual Au nuclei in the initial stages was only partly, or in some cases even slightly, controlled by spherical diffusion. Only when the density or the average size of Au nuclei exceeded a certain value was growth limited by linear diffusion of $Au(CN)_2^-$ ions. The latter is indicated by a decrease in current ($t > t_m$), which was not connected with coalescence of growing Au particles.

The occurrence of growth under mixed kinetic/diffusion control is simply illustrated as follows. Imagine that at $t = t_1 (t_1 < t_m)$ the density of Au nuclei is N and that growth of these nuclei is completely controlled by mass transport of $\operatorname{Au}(CN)_2^-$ ions. Then one should expect that the current is limited by linear diffusion from $t_{\rm m} = t_1 + \Delta t$ where Δt is the time in which the average diffusion length of Au(CN)2⁻ ions is of the same order of magnitude as the average distance between nuclei, *i.e.*, $(D\Delta t)^{1/2} \approx N^{-1/2}$. As an example, consider the current transient from Fig. 9 with the corresponding TEM images shown in Fig. 10. At $t_1 = 0.4$ s we have $N \approx 5 \times 10^{11}$ /cm². Using $D = 1.5 \times 10^{-5}$ cm²/s we obtained $\Delta t = 0.13 \,\mu s$, *i.e.*, the current maximum should be reached within 0.13 μ s from t_1 if growth was completely controlled by diffusion. The observation that the actual maximum occurs much later ($t_m \approx 1.2s$) thus indicates strongly that the growth rate is largely determined by some kinetic factor(s). Similar conclusions were obtained in other cases of Au deposition.

From the above it is clear that a quantitative analysis of the current transient (22) is extremely difficult, since the rates of both nucleation and growth depend on parameters such as overpotential, doping level, and light intensity. Furthermore, the kinetic factors determining the rates of growth and nucleation are expected to depend on the particle size as discussed previously.

Photoinduced electrodeposition.-Finally, we discuss the mutual dependence between the photocurrent and the dark current as observed during the initial stages of photoinduced Au electrodeposition on low-doped p-GaAs electrodes in the KAu(CN)₂/KCN solution (Fig. 11). The photocurrent is due to photoinduced formation of new Au nuclei and photochemical growth of existing Au nuclei. Obviously the latter process dominates the photocurrent since the critical size of newly formed Au nuclei is extremely small (<1 nm). When the light is switched off the current drops immediately, indicating a kinetically controlled dark current. The dark current is only due to growth of existing Au nuclei, since under the present conditions no nucleation occurs in the dark (Fig. 4a, curve a). The slow increase of the dark current is associated with an increase in the size of existing Au particles.

The dashed curves in Fig. 11 show that the dark current in the initial stages of illumination increases relatively fast. Consider for example in Fig. 11a the quantity of charge required to produce the Au deposits at points C and E, respectively. For point C illumination was stopped at t = 0.5s, whereas for point E illumination was stopped at t = 1.0s. The difference in the amounts of consumed charge at these points corresponds to the area ABCD. Imagine that this amount of charge is used to deposit Au on existing Au particles present at point C. This corresponds to the area CFGH (the line FG is chosen so as to equalize the area CFGH with the area ABCD). Then the amounts of consumed charge at points E and F are equal. However, the dark current at point E is much larger than at point F. This difference can only be explained by the occurrence of photoinduced formation and growth of new

Au nuclei between t = 0.5s and t = 1.0s. Thus the increase in the dark current caused by illumination is mainly associated with photoinduced progressive nucleation.

Conclusions

Cathodic Au deposition on p-GaAs electrodes from alkaline KAu(CN)₂ solutions is characterized by progressive nucleation and three-dimensional growth followed by coalescence of Au particles. Three mechanisms of electron transfer during Au nucleation were proposed. (i) Au nuclei are readily formed in a solution without excess CN⁻ ions due to hole injection from uncomplexed Au^+ ions. (ii) In a solution with excess CN⁻ ions, Au nucleation in the dark is also facilitated at higher doping levels ($>5 \times 10^{17}$ /cm³) of p-GaAs due to an increased probability of tunneling of valence band electrons to $Au(CN)_2^-$ ions. (iii) Au nucleation on low-doped ($<2 \times 10^{17}$ /cm³) electrodes in a solution with excess CN^- is only initiated by illumination and occurs by transfer of trapped photogenerated electrons from surface states within the bandgap to Au(CN)₂⁻ ions. In general, the nucleation rate increases when either the overpotential, the light intensity, or the doping level of p-GaAs increases. It is observed that the critical size of Au nuclei is smaller than 1 nm. Progressive nucleation occurs on bare p-GaAs parts at which the surface energy levels are not noticeably affected by neighboring Au particles.

Growth of Au nuclei formed in one of the above ways proceeds both in the dark and under illumination. The growing Au nucleus behaves like a microcathode at which Au(CN)₂⁻ ions are reduced. In the dark, valence band, electrons are transferred to Au particles, whereas under illumination photoexcited electrons may also facilitate growth. In both cases the electrons must tunnel through a small potential barrier whose magnitude is expected to depend on the size of the Au particle. The growth of individual Au nuclei is initially controlled both by kinetic factors and spherical diffusion of Au(CN)2⁻ ions. Only when the density or the average size of the nuclei exceeds a certain value is growth completely controlled by linear diffusion of Au(CN)2- ions.

p-GaAs electrodes covered with a sufficiently thick Au film behave like a Au electrode, indicating a small (<0.3V) Schottky barrier between p-GaAs and Au. This barrier is pinned so that potential changes appear across the Helmholtz layer at the metal-electrolyte interface.

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