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In Situ Deposition of Au on Plasma-Prepared GaAs Substrates

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In situ deposition of single crystal epitaxial and textured polycrystalline gold films on plasma-cleaned or plasma-etched GaAs substrates is accomplished in an ultrahigh vacuum integrated processing facility. Au/GaAs samples are characterized using reflection high energy electron diffraction, Auger electron spectroscopy, and ion channeling. Au crystallinity in films deposited at 100° C is shown to strongly depend on the GaAs surface cleanliness after plasma processing. Heating the substrate to 250° C after plasma processing subsequently yields epitaxial Au films; omitting the heating procedure results in polycrystalline Au films. The substrate thermal treatment removes residual physisorbed gas molecules and reaction products from the GaAs surface. Epitaxial Au films contain significantly less Ga and As on the free surface of Au than polycrystalline films, and no interaction between epitaxial Au and GaAs is observed.

Key words: Epitaxial Au, Au and GaAs, integrated processing

I. INTRODUCTION

Gold and gold alloy films are used extensively as ohmic contacts and interconnects for electronic, electro-optic, and opto-electronic gallium arsenide devices. The instability of the Au/GaAs interface due to interdiffusion at low temperatures is well known.[1] For example, immediately after room temperture Au deposition, Ga and As are observed on the Au surface where Ga accumulates over time and As evaporates from the surface.[2] It is presumed that As penetrates the metallization along Au grain boundaries or other film imperfections, liberating Ga which in turn enters the Au lattice via vacancy-mediated substitutional diffusion.[3] Subjecting Au films to high temperatures, such as used in contact alloying, further increases the diffusion of Ga and As through the films.[4,5] The reduction of As loss through the Au film has been shown to improve Au/GaAs ohmic contacts.[6]

The majority of previous investigations have characterized textured polycrystalline Au films that exhibit a preferred orientation on GaAs. However, epitaxial Au films on {001} GaAs have also been produced.[7-11] Epitaxial Au has been obtained by carefully cleaning impurities from the GaAs surface by chemical and thermal treatments and then depositing Au at a high substrate temperature.[7] In addition, on freshly prepared GaAs epilayers grown by molecular beam epitaxy (MBE), *in situ* Au epitaxial depositions have been achieved at room temperature[8,9] and 100° C substrate temperature,[10] or with vacuum annealing after deposition.[11] These studies have lead to a detailed understanding of Au film growth on $c(4 \times 4)$[7,9] and (2×4)[8,10] GaAs surfaces and the resulting interface electronic properties.

The epitaxial Au depositions on GaAs illustrate the necessity of operating completely within a clean vacuum environment. Further, the GaAs native oxide has been shown to have adverse effects on ohmic contact formation between gold alloys and GaAs, and hence improved uniformity and lower contact resistance result from an *in situ* cleaning procedure before metal deposition.[12] Therefore, integrated device processing accomplished in an ultrahigh vacuum environment offers the promise of high quality and high yield fabrication in addition to novel material formation. In an integrated fabrication process, a metallization step would likely occur after a plasma cleaning procedure[13] or a plasma etch.

In this paper we discuss *in situ* deposition of Au on plasma-prepared GaAs substrates. We find the GaAs surface condition after plasma processing determines whether single crystal epitaxial or textured polycrystalline Au films are deposited. Heating GaAs substrates to 250° C before Au deposition done at 100° C is found to be necessary for epitaxial Au films. Epitaxial Au films contain significantly less Ga and As on the free surface of Au than polycrystalline films, and no interaction between epitaxial Au and GaAs is observed. The reduction of Ga and As in epitaxial Au is consistent with the model of Ga and As interaction with Au.[3] Since prevention of Au loss has been shown to improve Au/GaAs ohmic contacts,[6] epitaxial Au contacts may possess improved electrical characteristics.

II. EXPERIMENT

The experiments are performed in an ultrahigh vacuum integrated processing facility which includes an electron cyclotron resonance (ECR) etch-

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ing chamber and a metallization MBE chamber, linked together by a transfer system with a base pressure of 2×10^{-10} Torr. (001) GaAs substrates, without any initial chemical treatment, are mounted on molybdenum blocks with indium solder and transferred into the ECR chamber for plasma processing. As discussed in a previous paper,[13] substrates are prepared at room temperature using either a hydrogen plasma treatment or a sequential combination of a hydrogen plasma and a $SiCl_4$ plasma etch, in order to remove the native oxide leaving a smooth and crystalline substrate surface. The plasma-prepared substrates are then transferred to the metallization MBE chamber (base pressure 2×10^{-11} Torr) for thermal treatment, Au deposition, and surface characterization by reflection high energy electron diffraction (RHEED). The substrate heating procedure entails heating the substrate to 250° C for 20 min. Au is deposited from an effusion cell at 0.1Å/sec at a substrate temperature of approximately 100° C. At various times the Au deposition is halted by inserting a shutter in front of the Au cell and RHEED patterns from the substrates are observed.

Analyses by Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS) in the ion channeling mode are performed in separate systems. The AES operating conditions for obtaining differentiated spectra are 5 kV excitation energy, 10 μA beam current and 2 eV modulation amplitude. The shapes and intensities of the peaks for Au (69 eV), Ga (1066 eV) and As (1225 eV) are recorded. Depth profiling is accomplished by sputtering the samples with a 4 kV Ar^+ ion beam rastered over a 4 × 4 mm area. The RBS ion channeling uses a collimated beam of 2.12 MeV He^{+2} ions with a constant dose of 4 μC for each spectrum. Backscattered ions are detected with particle detectors located at 104° and 162° from the incident beam direction. Aligned spectra are measured with the incident ion beam parallel to the ⟨001⟩ axis of the GaAs substrate. Random spectra are obtained with the substrate normal precessing at an angle of 4° about the incident beam direction.

III. RESULTS

In the following we discuss the plasma-preparation of GaAs substrates, the deposition of epitaxial and polycrystalline Au films, and subsequent characterization. Figure 1(a) and (b) show the RHEED patterns in the $\langle 1\bar{1}0 \rangle$ and ⟨110⟩ directions observed from GaAs substrates after plasma processing.[13] The streaky diffraction patterns are indicative of a smooth and oxide free surface.[14] The integer order (1 × 1) surface mesh reveals the surface atoms possess a disordered dangling-bond arrangement which disrupts surface reconstruction.[13] The particular substrate shown in Fig. 1(a) and (b) was prepared using only a hydrogen plasma; similar RHEED results are obtained from substrates prepared using the combination $H_2/SiCl_4$ plasma treatment.[13] In the former case the hydrogen plasma removes the native oxide from the original GaAs surface, while in the latter case the $SiCl_4$ plasma etches down into the substrate. In both cases the final surface is likely Ga rich. The substrate heat treatment is sometimes done before Au deposition on both plasma-cleaned and plasma-etched GaAs substrates, while other Au depositions occur immediately after plasma processing.

We next describe the deposition of single crystal epitaxial Au on thermally treated GaAs substrates. The GaAs RHEED features in Fig. 1(a) and (b) typically become narrower with less background intensity after the substrate heating procedure.[13] During the substrate annealing procedure, the chamber pressure increases to approximately 10^{-10} Torr, due to desorption from the substrate and molybdenum block, and eventually reduces to the base pressure. With the deposition of 0.5 nm of Au at 100° C, the streaky diffraction patterns are replaced by spotty patterns, indicating 3-dimensional island growth. After 3 nm of Au deposition, distinct streaky RHEED patterns which are different from those of GaAs are observed. These diffraction patterns become brighter and more distinct with further Au deposition. In Fig. 1(c) and (d) we show the diffraction patterns in the GaAs $\langle 1\bar{1}0 \rangle$ and ⟨110⟩ directions, respectively, obtained after deposition of 14 nm of Au. The identical growth sequence and RHEED results have also been observed for Au deposited on GaAs epilayers at 100° C with (2 × 4) or (4 × 4) surface reconstruction.[10] From transmission electron microscopy (TEM) diffraction, the following epitaxial alignment has been determined:[10] GaAs(001)//Au(110), GaAs$\langle 1\bar{1}0 \rangle$//Au $\langle 1\bar{1}0 \rangle$ and GaAs⟨110⟩//Au⟨001⟩.

Plasma-processed substrates which have not been thermally treated display different Au film formation. After 1 nm of Au deposition, faint spots are observed by RHEED; with continued Au deposition up to 100 nm thick, the spots become slightly elongated but remain faint. This behavior is consistent with a textured polycrystalline film that coalesces from initial Au islands which are partially ordered to the GaAs substrate. Summarizing, for Au deposition at 100° C, we find that regardless of whether that GaAs substrate has been plasma-cleaned or plasma-etched, a thermal treatment before deposition yields epitaxial Au, while omitting the heating step results in polycrystalline Au films. Note that Au depositions on plasma-prepared substrates at a substrate temperature of 30° C result in polycrystalline Au films, even with the substrate heat treatment.

Two Au/GaAs samples, one epitaxial Au, the other polycrystalline Au, were prepared as described above for characterization by AES and ion channeling. The AES peak intensities for Au, Ga, and As as a function of depth for epitaxial and polycrystalline Au/GaAs samples are shown in Fig. 2(a) and (b), respectively. The sputter time was converted to depth using the known thickness of the Au film and assuming the same sputter rate through the GaAs. The sputtering rate was consistently greater for the ep-

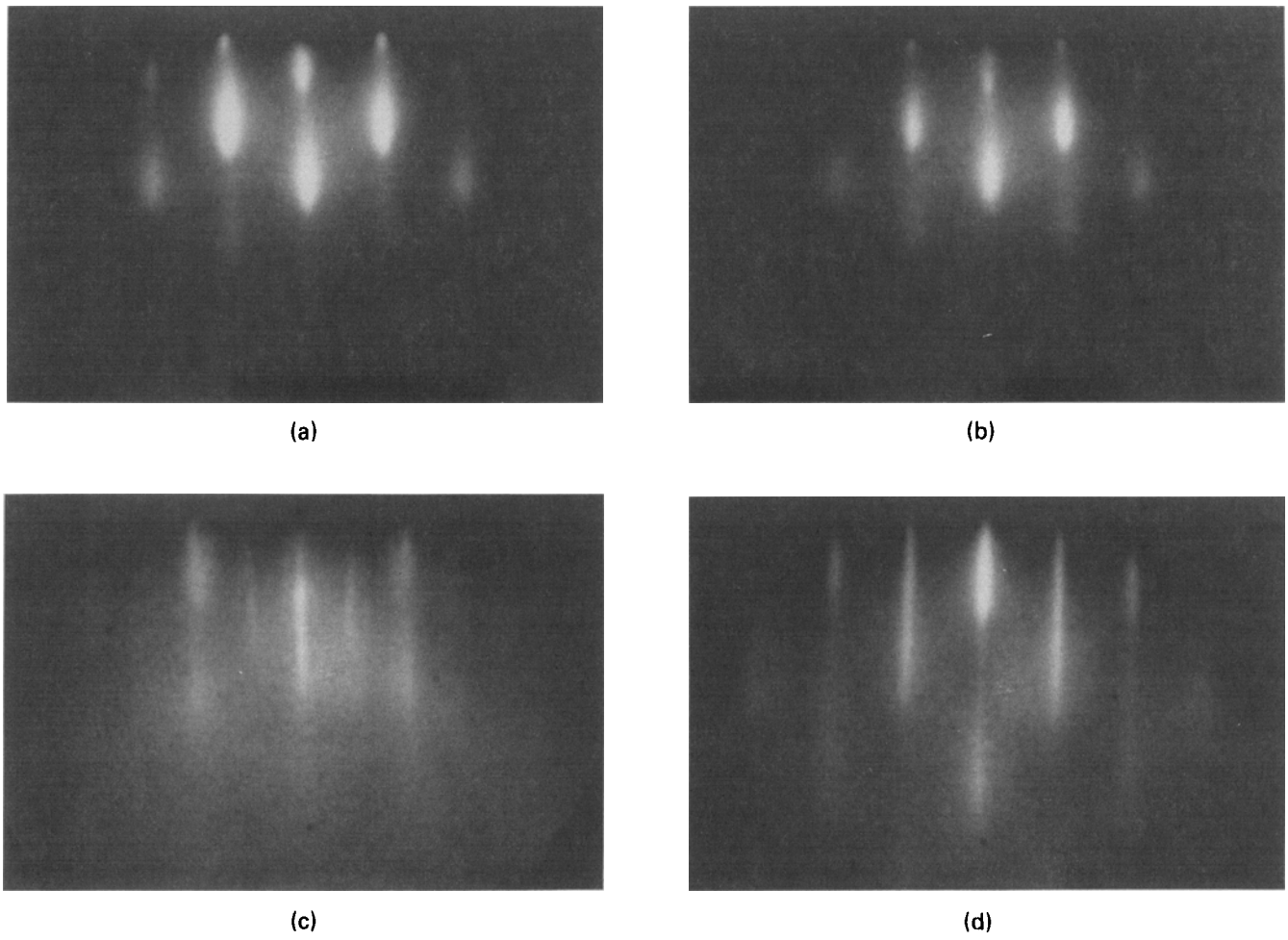

Fig. 1 — Reflection high energy electron diffraction patterns. (a) The $\langle 1\bar{1}0 \rangle$ direction and (b) the $\langle 110 \rangle$ direction of a GaAs substrate after hydrogen plasma treatment; (c) the $\langle 1\bar{1}0 \rangle$ direction and (d) the $\langle 001 \rangle$ direction of an 14 nm thick Au film on GaAs.

itaxial films. An identical depth is found at which Au, Ga, and As each exhibit half their maximum AES peak intensities. This depth is taken as the Au/GaAs boundary and is consistent with the abrupt Au/GaAs interface observed by transmission electron microscopy in other samples.[10] In Table I we give the peak intensity ratios of Ga and As to Au measured at the free Au surface. These ratios are proportional to the Ga and As surface concentrations. Notice significant accumulation of Ga is found within 1–3 nm of the top surface of the polycrystalline film in Fig. 2(b). We conclude that substantial quantities of Ga and As are present in the polycrystalline Au film as compared to the epitaxial sample.

In Fig. 3(a) and (b) we show backscattering spectra measured at 162° from the incident ion beam for the epitaxial and polycrystalline Au/GaAs samples, respectively. Both random and aligned spectra are shown for each sample. A Au peak and the Ga and As edge are apparent in each spectrum. From the Au peak area in the random spectrum, the film thickness is calculated to be 14 nm. The ratio of aligned to random scattering yield, χ_{min}, is a measure of the degree of crystallinity and for gold can range from 0.02 for single crystal Au to 1.0 for polycrystalline bulk Au. From the Au film peaks in Fig. 3(a) and (b), the measured χ_{min} values are 0.22 and 1.0, respectively. Note the GaAs χ_{min} values are 0.19 and 0.23 for the epitaxial and polycrystalline Au samples, respectively. Although the GaAs substrates are certainly single crystal, the χ_{min} values reflect the effects of beam dechanneling in the Au film, which also accounts for the slightly larger value from the polycrystalline sample.

In Fig. 3(c) backscattered spectra measured at 104° from the incident beam direction for the epitaxial and polycrystalline samples are shown. This glancing angle geometry with respect to the sample surface produces better depth resolution for the Au layer due to the longer ion trajectory through the film. Notice the Au peak from the epitaxial sample exhibits backscattering maxima at the two surfaces of the film, indicating the greater crystalline order in the interior of the Au film. The inset in Fig. 3(c) magnifies the region just above the GaAs substrate edge. The small feature evident at 1.75 MeV scattering energy for the polycrystalline sample is con-

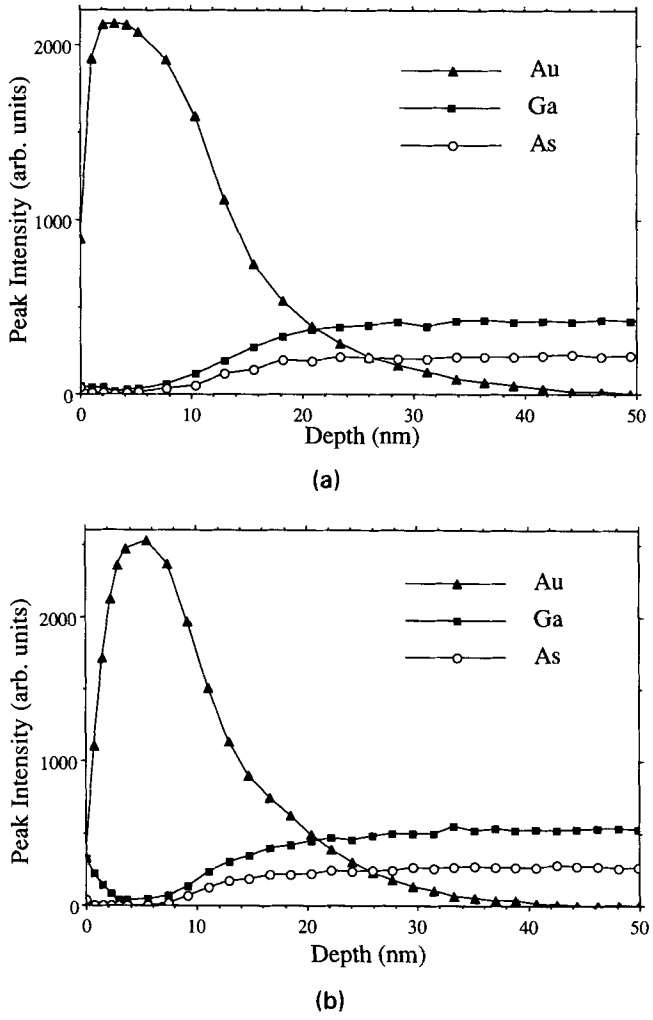

Fig. 2 — Auger electron spectroscopy depth profiles of Au/GaAs: (a) epitaxial Au film; and (b) polycrystalline Au film.

sistent with diffusion of Ga and/or As into the Au film. The epitaxial spectrum shows no evidence of interaction between Au and GaAs.

IV. DISCUSSION

The differences observed between Au films deposited at 100° C on substrates which are thermally treated or untreated arise from the initial GaAs surface condition. The substrate heat treatment leads to some surface annealing, as evident from the sharpened diffraction features. More importantly,

Table I. The Peak Intensity Ratios of Ga and As to Au Found by Auger Electron Spectroscopy on the Top Au Surface

Sample	Ga 1066 / Au 69	As 1225 / Au 69
Epitaxial Au/GaAs	0.05	0.04
Polycrystalline Au/GaAs	0.96	0.12

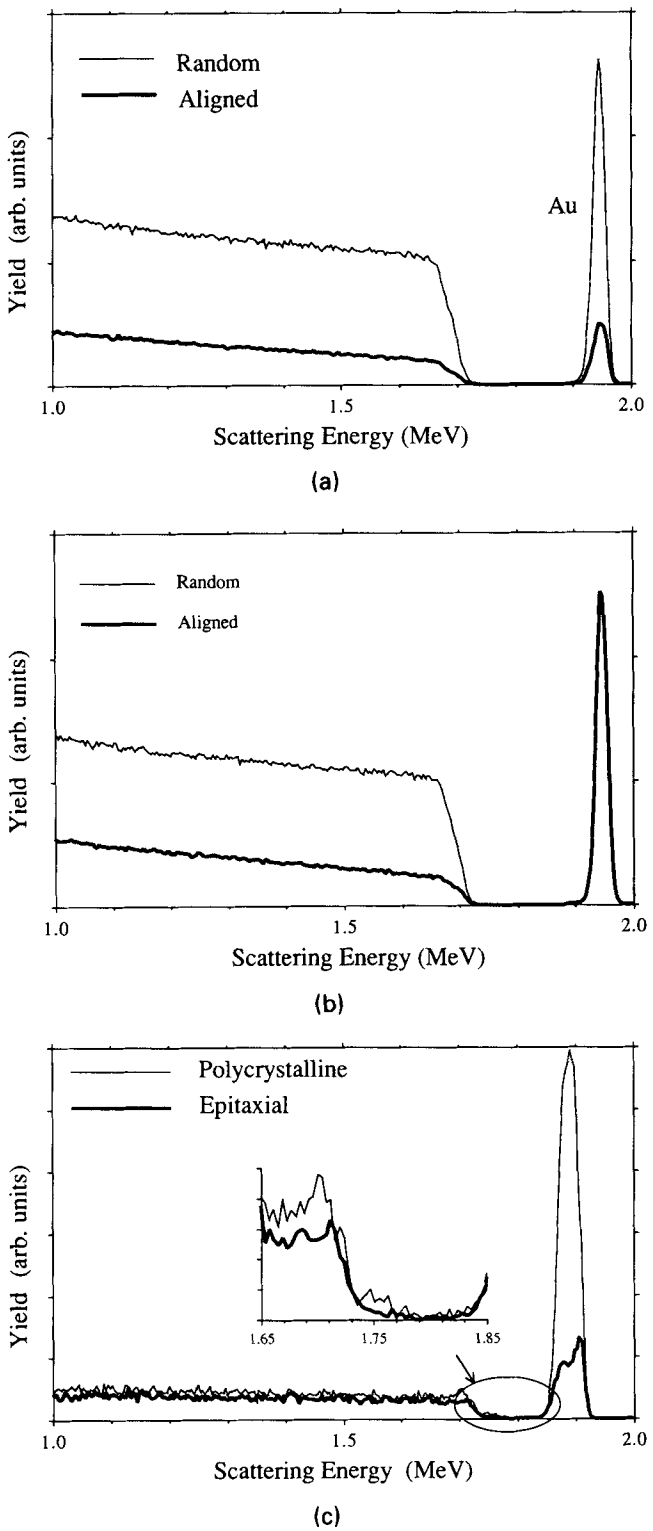

Fig. 3 — Ion channeling backscattering from Au/GaAs. Yields at 162° from the incident beam coincident and randomly aligned with ⟨001⟩ GaAs axis for (a) epitaxial Au and (b) polycrystalline Au samples. (c) Yields at 104° from aligned incident beam for epitaxial and polycrystalline Au samples.

residual physisorbed gas molecules and reaction products on the GaAs surface after plasma processing are removed as evident from the increase in the chamber pressure. The stages of growth for epitaxial Au on plasma-prepared and heated GaAs sub-

strates are consistent with the observations and models described in other investigations.[8–11] The deposition of a few monolayers gives a spotty diffraction pattern, indicative of the nucleation of Au clusters; after a few tens of monolayers, the Au islands coalesce into a continuous epitaxial layer. On substrates that are not thermally treated, residue from the plasma exposure results in an impurity-terminated surface which impairs perfect alignment of the initial Au islands on the GaAs surface. Hence, a textured polycrystalline film results. This behavior is analogous to the Au deposition on carefully cleaned GaAs substrates, where it was found that carbon contamination inhibits the formation of epitaxial Au films.[7]

The ion channeling data from the epitaxial Au film indicates that 22% of the Au atoms are displaced from their lattice position. This degree of disorder in the single crystal Au is consistent with the mismatch to the GaAs substrate: 27.8 and −2.0% in the $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ Au directions, respectively. The as-deposited epitaxial Au films described herein have comparable values of χ_{min} as annealed Au films on GaAs.[11] Note that Au deposited at 100° C exhibits equal χ_{min} as Au deposited on a MBE epilayer at room temperature followed by a 100° C anneal.[11] Polycrystalline Au films resulted from depositions at 30° C, irrespective of the substrate processing. Therefore, a substrate temperature of 100° C, during or after growth, appears to be necessary for epitaxial Au formation.

We do not find that Au deposition at 100° C leads to greater Ga and As incorporation into epitaxial Au films; in fact a significant decrease of Ga and As on the surface of epitaxial Au is observed as compared to polycrystalline films. The reduction of Ga and As in epitaxial Au is consistent with the model of their interaction with Au.[3] The decrease of surface As is consistent with the elimination of grain boundary As diffusion through epitaxial Au, which in turn impedes Ga dissolution into the Au. Therefore, it is not surprising that epitaxial Au films exhibit no interaction with GaAs, even at an elevated deposition temperature. Since prevention of As loss through an Au film has been shown to improve Au/GaAs ohmic contacts,[6] epitaxial Au contacts may possess improved electrical characteristics.

V. CONCLUSION

We make the following generalizations. First, a substrate temperature of 100° C during or after growth is required for epitaxial Au formation. Secondly, the crystallinity of Au films deposited at 100° C on GaAs is more dependent on the surface cleanliness than the crystalline perfection or surface reconstruction of the substrate. Thus epitaxial Au films are equally possible on plasma-cleaned, plasma-etched, or freshly grown GaAs surfaces. This illustrates the importance of surface cleanliness, one of the primary advantages of all vacuum integrated device processing. Finally, single crystal epitaxial Au films exhibit significantly less interaction with GaAs during and after film growth. By comparison, polycrystalline Au films show Ga and As incorporation, even when deposited a low temperature. Therefore, epitaxial Au/GaAs may inherently possess improved electrical properties due to the necessary clean interface and the superior Au film uniformity, purity and stability.

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