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Tungsten metallization onto InP prepared by rapid thermal low-pressure chemical vapor deposition of WF_6 and H_2

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Tungsten (W) films were deposited onto InP in a cold wall, rapid thermal low-pressure chemical vapor deposition (RT-LPCVD) reactor, using a tungsten hexafluoride (WF_6) gas reduced by hydrogen (H_2). W films of thickness 50–450 nm were deposited in the temperature range of 350–550 °C, pressure range of 0.5–4.5 Torr, and deposition rates up to 4 nm/s with an apparent activation energy of about 1.12 eV. The film stress varied depending on the deposition pressure, from low compressive (deposition at 0.5 Torr) to moderate tensile (deposition at about 4.5 Torr). Post-deposition sintering of the W films at temperatures up to 600 °C led to reduction of the resistivity with a minimum value of about 55 $\mu\Omega$ cm as a result of heating at 500 °C.

High-quality ohmic contact and barrier metallization schemes have become key features in III-V optoelectronic device manufacturing technology because of the need for long-term reliability performance. Among the preferred metals to be used in fabricating the ohmic contacts are the transition and refractory pure and alloyed elements such as Pt/Ti,[1] TiN_x,[2] and W.[3] The metals may be deposited both by physical and chemical deposition techniques, and this choice should be defined solely by the required application.

Tungsten is of special interest due to its relatively low resistivity (about 6 $\mu\Omega$ cm) and its stability, in particular its electromigration resistance. The various physical deposition techniques commonly used to deposit W films suffer some inherent deficiencies when applied to III-V compound semiconductors. Electron-beam evaporation uses a high beam energy, which leads to surface degradation and wide interactions and diffusion due to the heating of the substrate. Sputtering techniques may lead to some surface radiation damage. In addition, step coverage and conformality of the deposited layers, when depositing a blanket film or attempting via filling and narrow contact stripe coverage, are essential for the current device technology, and cannot be achieved by the physical deposition techniques.

As a result, the chemical vapor deposition (CVD) of tungsten has become a focus of interest in recent years. CVD of tungsten can be achieved by H_2 or SiH_4 reduction of WF_6 or WCl_6, or by the pyrolysis of $W(O)_6$. In contemporary blanket tungsten CVD, WF_6 is used almost exclusively as the W source reduced by either H_2 or SiH_4, or a mixture of the two.[4–10] Tungsten has been deposited in a selective manner, as well, into exposed silicon regions in a SiO_2-masked surface and various mechanisms have been suggested for the initial nucleation of the tungsten in the holes.[11–13] The selective deposition is an extremely sensitive process to the deposition conditions, such as pressure and temperature, and in addition, is affected by any slight change in the substrate surface chemistry. Metallic contamination on the dielectric surface or chemistry surface poisons (such as CrO_2F_2) on the semiconductor surface may prevent the selective deposition mode.

The purpose of this work is to evaluate the type and quality of tungsten films deposited from a WF_6 source and reduced by H_2, onto InP, by means of a cold wall rapid thermal low-pressure chemical vapor deposition (RT-LPCVD) reactor.

W films were deposited onto (100) InP substrates by the RT-LPCVD technique using an A. G. Associates Heatpulse CVD-800™ system. This is a low-pressure, load-locked, horizontal and laminar flow reactor, heated by two sets of high-power halogen-tungsten lamps (12 lamps of 1.5 kW each) and is capable of processing a single wafer under inert, hazardous or corrosive ambients.[14]

WF_6 reduced by H_2 and diluted in Ar was used as the reactive gas mixture to deposit the W films. The gas mixture was flown into the chamber over the loaded cold substrate for at least 2 min before turning the lamps on. At the end of the deposition cycle, the substrates were cooled down in the reactor under a H_2 flow for 2 min before they were unloaded to the loadlock. The deposition conditions were as follows: The chamber pressure was varied in the range of 0.5–8.0 Torr, the temperature was kept in the range of 350–500 °C and the gas flow rates of Ar, H_2, and WF_6 were in the ranges of 25–500, 250–2500, and 10–50 sccm, respectively. The wafers were loaded, immediately after being de-oxidized in 10:1 H_2O:HF solution and degreased by means of warm chloroform, acetone, and methanol, into the CVD-800 loadlock chamber. A vacuum of better than 9×10^{-6} Torr was achieved after about 30 s of pump down.

Various analytical techniques, such as transmission electron microscopy (TEM) and Auger electron spectroscopy (AES) were applied to characterize the properties of the RT-LPCVD W films. Deposited film thicknesses were measured using a Dektak™ stylus profilometry system and were verified by scanning electron microscopy (SEM) cross section. *In-situ* stress measurements were performed using the Flexus 2-300S thin-film stress measurement system, at elevated temperatures, up to 500 °C.[15] For electrical measurements the transmission line method (TLM) and four-point probe techniques were used to measure contact resistance and film resistivity, respectively.

Evaluation of the influence of the various parameters associated with the RT-LPCVD W film, such as the Ar,

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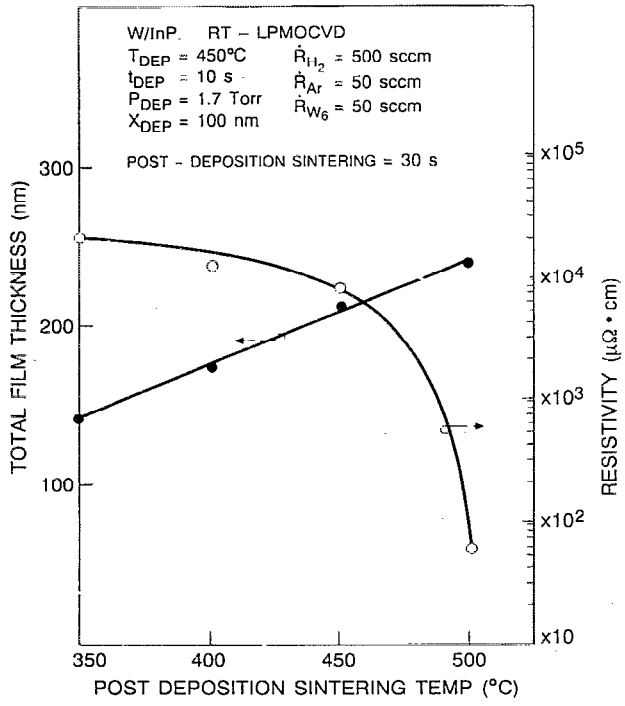

FIG. 1. RT-LPCVD W film thickness and resistivity as a function of the post-deposition sintering temperature.

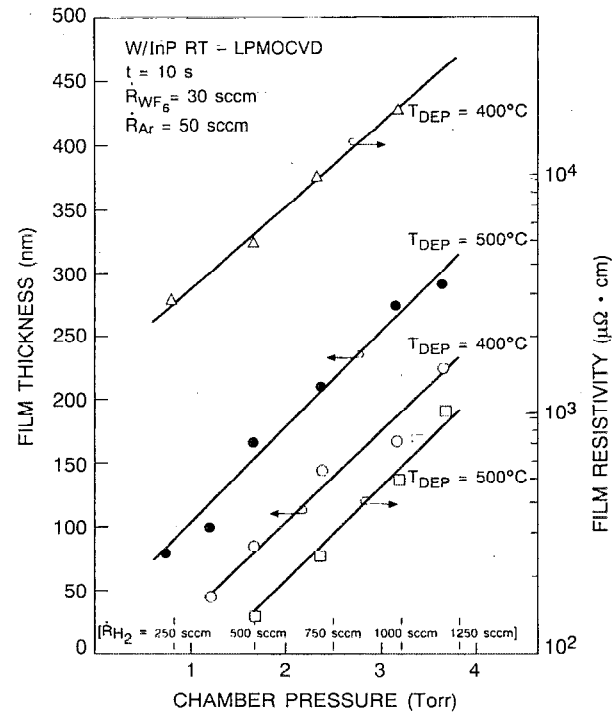

FIG. 2. RT-LPCVD W film thickness and resistivity as a function of the total chamber pressure and H_2 flow rate during deposition.

H_2, and WF_6 gas flow rate, chamber pressure, deposition temperature, and duration, and post-deposition sintering temperature and duration, on the film deposition kinetics and film resistivity was carried out. The growth rates were calculated from the thickness of the deposited layers. From initial experiments, the best deposition conditions were defined to be: gas mixtures of 1500 sccm H_2, 50 sccm Ar, and 20 sccm WF_6 (H_2:WF_6 of 75:1) and total pressures of about 4.5 Torr. In attempts to investigate the appropriate deposition temperature, samples were run at temperatures from 300 to 600 °C. Deposition was never observed for temperatures lower than 400 °C. Temperatures higher than 500 °C, however, led to sporadic and uncontrolled deposition. Thus a few sets of samples were used to investigate the actual influence of temperature on deposition kinetics, in particular in the range of 400–500 °C, in intervals of 10 °C. Each set of samples was evaluated for deposition durations of 2–20 s. From this study the film deposition apparent energy was calculated to be about 1.17 eV/mol. All these films, as-deposited were found to have resistivity in the range of about 8×10^3–2×10^4 $\mu\Omega$ cm.

In an attempt to reduce the high resistivity of the W films, an *in situ* post-deposition sintering process was applied subsequent to the deposition under a vacuum of better than 1×10^{-5} Torr in the same chamber. Figure 1 shows the significant reduction of the W film resistivity from the initial value of about 2×10^4 $\mu\Omega$ cm while deposited at 450 °C, to about 55 $\mu\Omega$ cm as a result of sintering this sample for 30 s at 500 °C. In particular, a significant reduction is observed for 30 s sintering at temperatures that exceed 450 °C. In addition, this figure shows the thickness of the reacted layer measured by means of TEM. This layer doubled its as-deposited thickness upon heating at 500 °C for 30 s. The nature of the reacted layer was evaluated and will be discussed later on.

The correlation between the thickness and resistivity of W films that were post-deposition sintered at 500 °C and, both the H_2 flow rate and the chamber pressure is given in Fig. 2. This data reflects two deposition temperatures, 400 and 500 °C, and gas flow of 30 sccm of WF_6 and 50 sccm of Ar. A linear correlation between the thickness of the deposited layer and the total chamber pressure, regardless of the deposition temperature, is observed with a slope of about 60–90 nm/Torr. A strong dependence of the resistivity on the total chamber pressure at all deposited temperatures, was observed, revealing an increase of about a factor of 2 in the resistivity per increase of 1 mTorr in the chamber pressure.

The thermodynamic analysis of the W-InP reactions is very complicated due to the lack of phase diagrams for both the In-W and P-W binary systems. Some data, however, is available,[16] predicting the unstable nature of the W-InP system. For the case of P-W, two compounds were reported, the WP_2 and WP_3, which are polymorphic forms and thus metastable at low temperature and normal low-pressure conditions. Those compounds contain 68 and 85 at. % of P, respectively, and are very reactive at the given RT-LPCVD condition of 350–500 °C and 0.5–10 Torr. For the In-W system, no information on the existence of intermetallic phases has been reported.

Extensive TEM work was done to evaluate the initial as-deposited layer microstructure and composition. Figure 3 shows the flat on bright field (left side) and dark field (right side) images, as well as the selected area electron diffraction (SAD) pattern of W films that were deposited

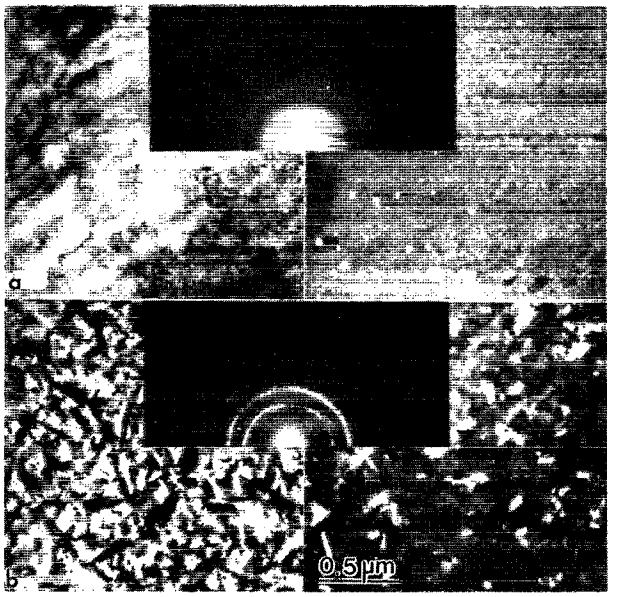

FIG. 3. TEM plan view bright field (left side) and dark field (right side) images, as well as SAD patterns of W RT-LPCVD films deposited at the same conditions of $Ar:H_2:WF_6$ flow rates of 50:1500:30 sccm and pressure of 4.5 Torr at temperatures of (a) 450 and (b) 500 °C.

at the same deposition conditions of $Ar:H_2:WF_6$ flow rate of 50:1500:30 sccm at total chamber pressure of 4.5 Torr, however with different temperatures of 450 °C [Fig. 3(a)] and 500 °C [Fig. 3(b)]. In both cases, no post-deposition sintering was applied. The film that was deposited at 450 °C shows an amorphous W film structure, with some spreading of a P-W polycrystalline binary unidentified phase. The sample that was deposited at 500 °C, however, was deposited in a polycrystalline structure and comprised a preferred oriented [see SAD of Fig. 3(b)] polycrystalline needle-shaped phase which was found by EDX to contain a significant amount of In and P in addition to W. This phase is also an unidentified phase and current work is proceeding to define its crystallographic structure.

TEM analysis of the above samples that were sintered after deposition, were done. Post-deposition sintering at 450 °C for 30 s and at 500 °C for 30 s led to the formation of the same needle-shape ternary phase with a preferred oriented grain growth, as was observed earlier in the sample that was deposited at 500 °C.

One can see that the needle-shape phase grain formation may be driven by either high deposition temperature, above 450 °C or by post-deposition sintering at temperatures of 450 °C or higher. As a result, the currently unidentified In-P-W ternary needle-shape phase is found to occupy a large fraction of the initial W layer. This phase formation is likely to be the origin of the abrupt decrease in the film resistivity down to very low values of 50-80 $\mu\Omega$ cm.

In summary, we have demonstrated the deposition of W films onto InP semiconductor substrates by means of the RT-LPCVD technique, using WF_6, H_2, and Ar gases. The required deposition temperature was higher than 400 °C and pressures had to be higher than 0.5 Torr. Increasing the deposition temperature led to a reduction in the film resistivity, but a post-deposition sintering cycle for 30 s at temperatures in the range of 400–500 °C was required in order to bring the film resistivity down to an acceptable value of less than 100 $\mu\Omega$ cm. These heat treatments led to a reaction between the W cap layer and the InP substrate resulting in the formation of the yet unidentified In-P-W ternary needlelike phase. Once the film undergoes these reactions upon post-deposition sintering it becomes a very stable and low-stress film. The performance of laser devices that were metallized with this tungsten scheme will be discussed elsewhere.

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