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Electron beam stimulated chemical vapor deposition of patterned tungsten films on Si(100)

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Electron irradiation of WF_6 films on Si has been studied using scanning Auger and electron microscopic techniques. In contrast to metal organics, electron stimulated decomposition of WF_6 is found to result in formation of pure W deposits; patterned films are formed by scanning the focused electron beam. The morphology of the films is particulate and the manner in which this originates is discussed.

A number of methods are currently being explored for the maskless formation of high-resolution patterned metal films on semiconductor materials. These include the decomposition of volatile molecular precursor compounds in the vicinity of the substrate surface, using focused photon, ion, and electron beam sources[1–6]; such approaches possess obvious potential application to microelectronics fabrication. Electron-induced deposition of metals from metal carbonyl precursors has been studied in some detail.[7,8] A major problem revealed is the lack of selectivity in the chemical bonds ruptured by high-energy electrons. Thus in the case of $Fe(CO)_5$ films, electron irradiation was found to break Fe–C and C–O bonds with approximately equal probability, resulting in the deposition of iron carbides, rather than iron. In this letter we present results for the deposition of W films from WF_6, where such problems are not observed; pure W films are deposited by electron irradiation and delineated by scanning the focused beam across the surface.

All experiments were carried out in a stainless-steel ultrahigh vacuum chamber, pumped by an 800 l/s titanium ion pump, in which base pressures below 10^{-10} mbar were achieved before experiments commenced. The chamber was equipped with scanning Auger microprobe and Ar^+ ion etching facilities. The polished (100) oriented Si wafer was degreased by rinsing in acetone prior to insertion in the vacuum chamber and was cleaned *in situ* by slow heating and cooling between 300 and 1500 K.[9] Subsequent Auger analysis indicated carbon as the only trace surface contaminant, with C(270 eV):Si(92 eV) Auger peak-to-peak signal height ratios below 0.02 in the differential spectrum. Previous low-energy electron diffraction studies[7] have revealed that a sample prepared in this way exhibits an ordered (100) (2×1) reconstructed superstructure. The Si wafer could be cooled to 77 K and exposed to WF_6 vapor by means of a differentially pumped dosing source which developed a 10^3 pressure enhancement in the vicinity of the sample. All Auger spectra and electron beam deposition experiments employed a 5-keV, 3-μm spot size electron beam incident on the sample at 45° to the surface normal and operated at current densities of 10^3 A m^{-2}. Secondary electron microscopy (SEM) was carried out *ex situ* after exposure of the sample to the atmosphere.

Although no adsorption could be detected at 300 K after exposure of the sample to the WF_6 vapor, thick (1–5 μm) WF_6 films could be straightforwardly condensed on the sample at 77 K. The effects of electron beam irradiation on the phases thereby formed were examined by Auger spectroscopy and results are presented in Fig. 1. In Fig. 1(a), changes in the spectra of the W NNN 160–180 eV Auger transitions induced by electron irradiation are illustrated, while corresponding data in Fig. 1(b) relate to the F KLL 650 eV Auger transition. It is apparent that fluorine rapidly desorbs from the surface during electron irradiation and a concomitant increase in the surface W concentration is observed. Although not of central interest here, shifts in peak energies during electron irradiation are also detected, reflecting the change in chemical state as the WF_6 film is decomposed. The electron beam produces a negligible temperature rise so the reaction observed must be stimulated by electronic processes rather than by thermal excitation. While the above data refer to 4 μm films average thickness as observed in SEM, the results were insensitive to WF_6 coverage down to submonolayer quantities. At these low coverages, the Auger peak profiles were characterized of pure W and Si phases, indicating that WSi_2 (which is the product of the thermal reaction) is not formed during the process. After

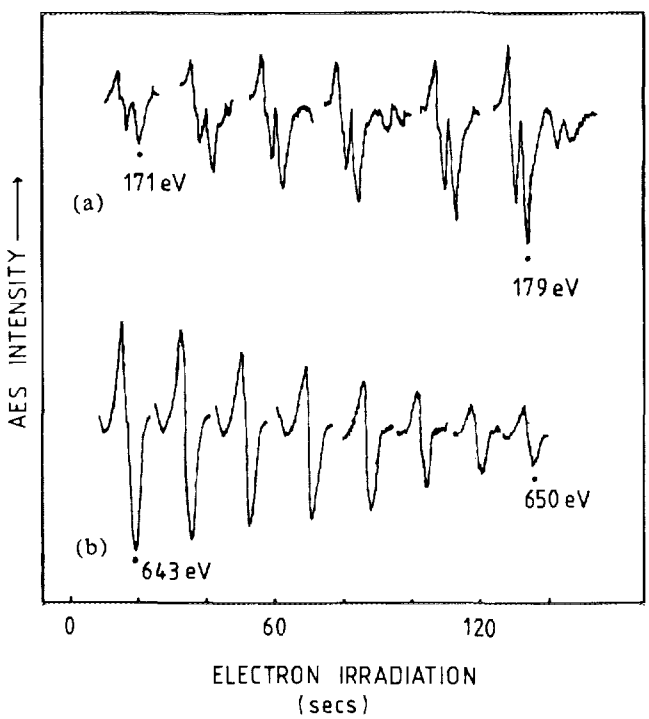

FIG. 1. Variations in Auger spectrum of WF_6 film during electron irradiation. (a) W NNN 160–190 eV spectral region, (b) F KLL 650 eV spectral region.

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electron irradiation, no fluorine whatsoever is observed in the surface layers at the 1% monolayer detection levels typical of Auger spectroscopy and so it can be concluded that the method is viable for the production of pure W films.

By repetitively scanning the electron beam over the surface it is possible to produce delineated deposits and scanning Auger and electron microscopic images of such thick (2 μm) deposits are shown in Figs. 2 and 3. Due to vibration in the sample holder (associated with the passage through it of liquid nitrogen), the width of the tungsten lines is 200 μm; however, single electron scans (which produced much thinner W lines) produced linewidths reflecting the 3 μm spot size of the exciting beam. SEM photographs of the deposits reveal that the film is strongly featured and particulate in nature; in line with this is the observation that the resistivity of the deposits is estimated to be approximately two orders of magnitude greater than bulk tungsten.

While electron irradiation of metal carbonyls[7,8] produces highly contaminated deposits, it is apparent from the present work that the corresponding process using volatile metal halides represents a much more viable method for depositing patterned metal layers since high film purities can be achieved. The morphology of the thick deposits formed here is poor, but this probably arises from our particular experimental setup which requires adsorption of the WF_6 film prior to irradiation. The reaction mechanism is likely to involve the formation of pure W nuclei (since no F is present in the final deposit) within the decomposing WF_6 phase, which increase in size during irradiation, producing particulate deposits. This explains why the morphology of the final film is so different from the uniform WF_6 layer initially deposited. An alternative approach which would be expected to produce better results would be to electron irradiate continuously during adsorption at pressures/substrate temperatures corresponding to low equilibrium coverages. Our data indicate that the efficiency of electron stimulated desorption is such in this configuration that practically useful growth rates (for "direct writing") of 100 μm s^{-1} could be developed at readily achieved current densities of 10^6 Am^{-2}, with beam voltages of 6 keV. The characteristics of the electron beam driven process are rather different from those well documented for the thermal chemical vapor deposition of W films on Si from WF_6.[10–14] In particular, since the thermal reaction occurs via formation of SiF_4, limiting film thicknesses of ~ 10 nm are observed with Si etching occurring to depths on a similar scale; since the electron stimulated reaction involves the simple rupture of the WF_6 molecule, very

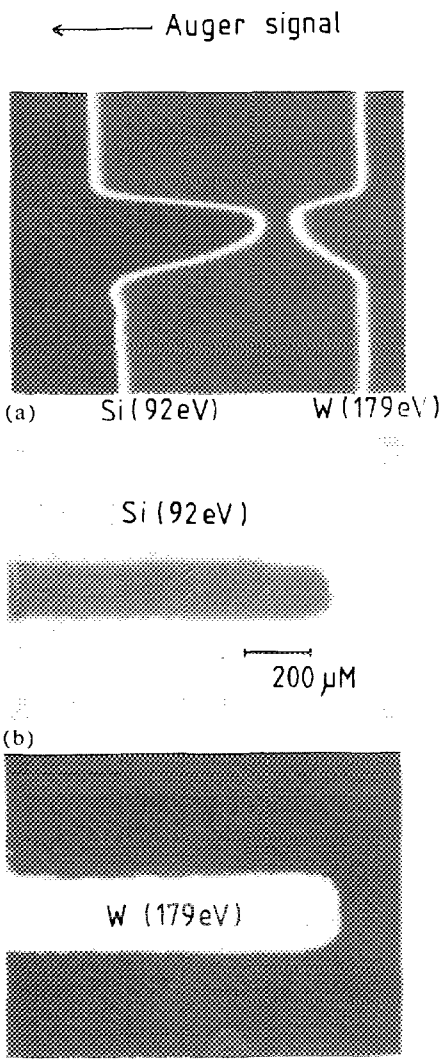

FIG. 2. Scanning Auger micrographs indicating the localized nature of the W deposit. (a) Line scans across deposit, perpendicular to direction of delineation, (b) Auger map monitoring Si (92 eV) transition, (c) Auger map monitoring W (79 eV) transition. Light regions correspond to high elemental concentrations.

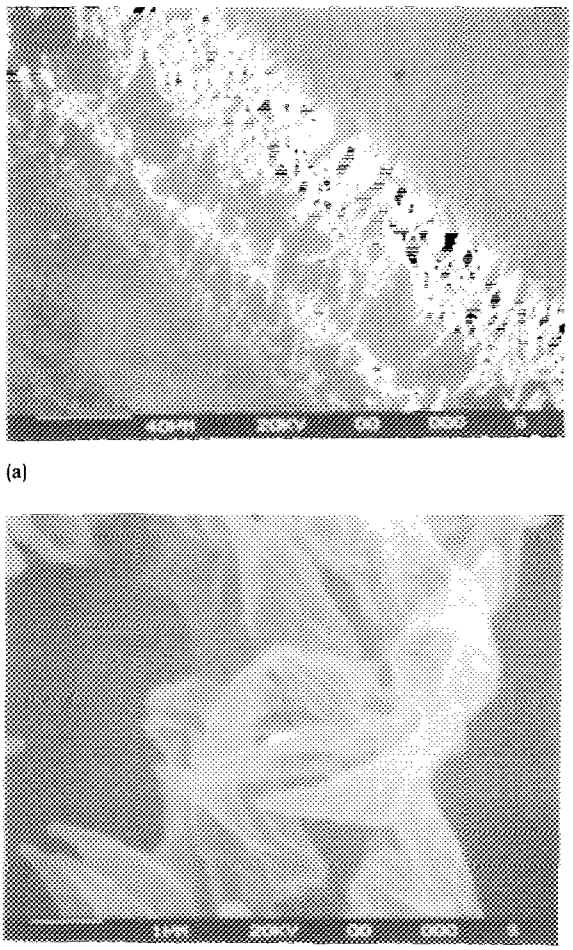

FIG. 3. Scanning electron micrographs, at differing resolutions, of the W deposit illustrating the strongly featured morphology.

little Si etching is expected to take place and films of unlimited thickness can be readily prepared.

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