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Metal-Organic Chemical Vapor Deposition in a Transmission Electron Microscope

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Background incl. aims

Using environmental transmission electron microscopy, researchers can observe - with high resolution and in real time - transformations and reactions under realistic conditions. Such studies benefit from precise control, monitoring, and variability of ambient gas, potentially including multiple independently controlled species to which a sample is exposed at the same time. This represents a challenge for ETEM analysis and has required the design of systems that integrate the capabilities of advanced crystal growth instrumentation with the specific requirements of TEM to allow elevated sample pressure and temperature, as well as a better understanding how the environment influences the analysis and vice versa. To address these challenges, we developed an ETEM system based on a Hitachi HF3300S instrument, which is integrated with a metal-organic chemical vapor deposition (MOCVD) system designed for real-time investigation of crystal growth processes of semiconductor nanostructures[1].

Here, we demonstrate how the design of the ETEM-MOCVD instrumentation enables independent control of the gas composition and flow that reaches the heated sample region, as well as rapid adjustments of the gas supply. We focus on the implemented solutions used for controlling gas concentration and pressures in the system and at the sample region. Solutions for calibration and monitoring partial pressures as well as total pressure in the microscope and at the sample are presented and evaluated, together with pressure correction factors of the pressure gauges for nitrogen (N_2), arsine (AsH_3), and phosphine (PH_3). In addition, we explore the influence that the temperature and gas supply to the microscope itself have on imaging and analysis, and conversely, how the imaging via electron beam influences the experiment. Effects of temperature and gas environment on spatial resolution are quantified, and we also demonstrate and quantify how X-ray energy-dispersive spectroscopy (EDS) analysis is influenced by the local reactive sample environment.

Methods

The ETEM is based on an image corrected Hitachi HF-3300S 300 kV TEM, with additional ion pump and differential pressure aperture. The gas handling system is custom built but based on industrial standard mass flow controllers, pressure controllers and vapor concentration measurement units (HORIBA). Nine different gases are controlled via the gas handling system, primarily for III-V semiconductor growth: trimethylgallium (TMGa), trimethylindium (TMIn), trimethylaluminum (TMAl), trimethylantimony (TMSb), AsH_3, PH_3, nitrogen, hydrogen, and oxygen. Other gases are possible by either replacing any of the existing sources, or by using external gas delivery and leak valves. Heating is done using MEMS heating chips.

Results

The design of the gas handling system and particularly the ability to dilute the precursor species with additional high flow of H_2 allows for a very wide range of precursor flows and partial pressures to be achievable, spanning over four orders of magnitude (approximately 4 × 10-6 to 0.1 Pa of TMGa, or 7×10^{-5} to 2 Pa of AsH_3). These partial pressures are comparable to conventional MOCVD growth of binary semiconducting nanostructures.

Since the microscope is of an open design with local gas injection close to the heated area of the holder, a local higher pressure at the holder compared to the column pressure gauge location is expected. Using a MEMS heating chip as a pulsed Pirani gauge, we correlate pressure at the holder to the microscope column pressure. Depending on gas delivery method (via gas injection holder or side port injector) and holder tilt, pressure at the MEMS chip was found to be 1.6 to 2.8 times higher than column pressure gauge. If using additional lid on gas injection holder, pressure at the MEMS chip was found to be 200 times higher than the column pressure.

Achievable spatial resolution during gas exposure on a heated MEMS chip was estimated using Young's fringes. Measured resolution is slightly worse than the 0.86 Å achievable under optimized conditions[2], mainly due to stability of the holder and MEMS chip. Elevated temperature and gas exposure had a very minor effect on resolution.

Increasing temperature on the SiNx based MEMS chips, the thermal radiation of the chip increases. Such thermal radiation affects the EDS measurement mainly by increasing the strobe peak intensity, but at high enough chip temperature also energy shift of strobe peak and elemental peaks.

Conclusion

We present a system that merges an environmental TEM with an MOCVD setup for real-time study of crystal growth. The open holder design allows for a wide sample tilt range, quick gas switching, and various analysis techniques. The gas handling system replicates standard MOCVD conditions and is flexible for different gas pressures, flows, and precursor types. We found no significant effect of heating or gas pressure on spatial resolution, and minimal interaction of the electron beam with the gas.

Keywords:

ETEM, in-situ, MOCVD, semiconductor

Reference:

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