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Man-made Superlattice Crystals

Abstract: Multiple closely spaced layers of $GaAs_{1-x}P_x$, which approximate a one-dimensional crystalline superlattice, have been created by periodically pulsing PH_3 into an AsH_3-PH_3-Ga-HCl vapor-growth apparatus. The phosphorus mole fraction varies between maximum and minimum values with a period typically less than 200Å. Structures with up to 150 such layers have been produced. The crystal growth process and methods of characterization are discussed briefly.

Since announcement of the possibility of detecting negative differential conductance in a crystalline structure with a built-in periodic variation in the lattice potential,[1] much interest has centered around various possible ways to create such a structure in the laboratory. Two of the possibilities considered are evaporation of alternate layers under high vacuum and use of naturally occurring alternations in crystal properties such as periodic doping gradients. But to date the only successful approach has been with crystal growth from the vapor phase in which layers of $GaAs_{1-x}P_x$ with alternating values of x (the mole fraction of phosphorus) are deposited epitaxially onto GaAs substrates by rapidly and reproducibly altering the phosphorus content of the vapor source. The multilayered structure thus produced can be regarded either as a series of closely spaced heterojunctions or as a one-dimensional superlattice in the direction of crystal growth, with a period of the order of 40 or so normal unit cells. In the ideal case of no gaseous or solid interdiffusion, the composition of part of a layer approaches that of pure GaAs (i.e., $x = 0$) and rises abruptly to $x = 0.5$ in the other part. In the real structure the variation of x within each single layer, although very difficult to measure exactly, is estimated from x-ray data to be from about 0.1 to about 0.4.

Figure 1 shows an electron micrograph of one such superlattice structure after preferential etching. The fine lines represent adjacent sections of the crystal that are phosphorus-rich and phosphorus-poor, respectively, with a peak-to-peak spacing of about 140Å. The topography is developed by cleaving the specimen normal to the plane of the parallel crystal layers and subjecting the cleaved surface to an etch consisting of HF, H_2O_2 and H_2O. Some of the layers have etched more deeply than others and a roughly diagonal undulation can be seen on the cleaved surface. These coarser features may be due to slight fluctuations in various crystal growth or etching parameters or to lattice strain effects. The most significant feature, however, is the uniformity of the fine structure, i.e., the superperiod.

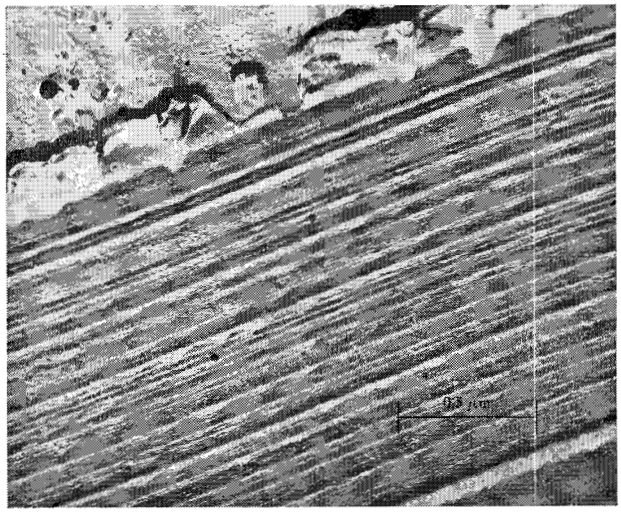

Figure 1 Transmission electron micrograph (36,000×) of a 120-layer $GaAs_{1-x}P_x$ superlattice with 140-Å spacing. The rough layer atop the superlattice is a result of the replication process.

The electron micrograph was obtained in a Philips EM 100 transmission electron microscope. To obtain a

replica of the superlattice chip for transmission microscopy, the cleaved cross section was first pressed face down against soft pressure-sensitive tape. A small open-ended cylinder enclosing the specimen was also pressed against the tape and Araldite epoxy cement was flowed gently over the back of the wafer. Upon hardening, the tape was stripped off the front to expose an epoxy surface flush with the face of the specimen. The normal replication technique was then applied to the encapsulated sample.[2]

Vapor deposition of multiple thin films of metals and epitaxial growth of a series of different semiconductor layers are not new concepts. The novelty of the present process lies in the large number of such layers that can be produced with relative ease, yet can be maintained thin and distinct from one another and completely monocrystalline throughout the whole series. We have grown from 15 to 150 layers at a time with no trouble arising from increasing the number. Indeed, there is some evidence that the perfection of the layers increases with increasing number. Average superlattice spacings have been observed that vary from a minimum of 110Å to more than 1000Å. The constancy of spacing and the degree of parallelism of the layers are the two chief goals of the work, since they are among the prime determinants of whether the superlattice will exhibit the properties predicted in Ref. 1. Figure 1 shows an area of one of the growths where the spacing did not vary visibly over a thickness of 120 layers and a width of the order of several mils. Mathematical analysis of x-ray spectra from a similar specimen indicated that the constancy of the period in that case is probably of the order of one percent.

The semiconductor $GaAs_{1-x}P_x$ is well known for its p-n junction electroluminescence and is being used in industry as a basic material for the fabrication of alphanumeric displays.[3] Convenient apparatus for growing this material from the vapor has been described by Tietjen and Amick.[4] However, contrary to the usual intent, which is to produce a crystal in which x is constant, superlattice growth requires that we purposely create abrupt discontinuities in the phosphorus mole fraction and, in effect, stack the discontinuities one upon another at intervals of a few hundred angstroms. Consequently we have replaced the usual mixing chamber, where AsH_3 and PH_3 are homogenized, with an injection system (Fig. 2) that keeps the arsenic and the phosphorus separated until a fraction of a second before crystal growth. The vapor growth is carried out at about 750°C, a temperature at which the layers, once formed in the solid state, do not appreciably interdiffuse.

The principal element of the injection system is a three-way solenoid valve through which the PH_3 is diverted to the outside except during the instants of injection into the reaction mixture. By electronic control of the duration of the injection cycle, not only the overall spacing of the layers but also the proportion of phosphorus-rich to phosphorus-lean sections can be tailored. In principle, by making the injection cycle shorter and shorter, the spacing could be made even smaller, but this process breaks down when the volume of gas going through the valve in a cycle becomes comparable to the effective internal volume of the valve itself. At this point a pumping action begins to dominate, and this action occurs in the present case for pulse rates of less than one per second. Currently we use a two-second injection cycle with a one-second square-wave pulse. This results, when the overall growth rate is 40 μm/h, in a spacing of 225Å.[5]

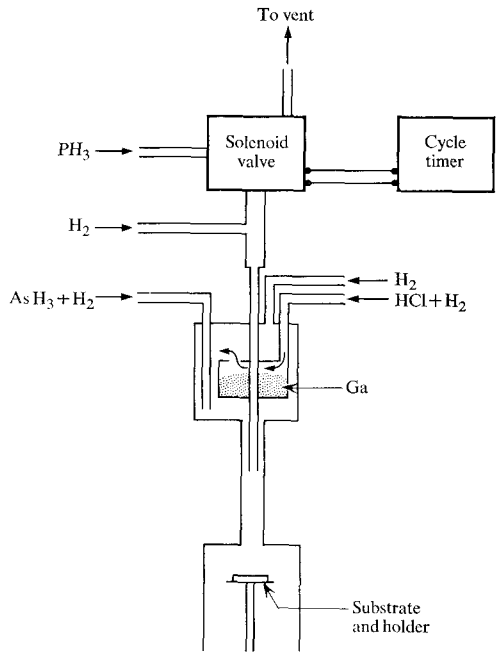

Figure 2 Injection system with three-way electromechanical valve for growing layers of alternating composition.

It is clear that in order to achieve the objective of flat and parallel layers with constant spacing in the hundred-angstrom range, the growth rate must be reasonably low and, above all, constant. We have observed that the growth rate increases with increasing phosphorus concentration under some conditions, but not always. Elucidation of these conditions and how the growth rate can be more closely controlled is the subject of continuing research. Other pertinent observations are that lateral uniformity is dependent on the choice of crystal orientation and vapor composition. The best results so far with respect to planarity have occurred with the (311) substrate orientation. If less than a certain critical chloride concentration (whose value also depends on the orientation) is maintained in the reactor, the layers tend to be nonplanar.

References and notes

1. L. Esaki and R. Tsu, *IBM J. Res. Develop.* **14,** 61 (1970).
2. *Techniques for Electron Microscopy,* edited by D. Kay, Charles C. Thomas Publishing Co., Springfield, Illinois 1961.
3. R. A. Burmeister, Jr., G. P. Pighini and P. E. Greene, *Trans. TMS-AIME* **245,** 587 (1969).
4. J. J. Tietjen and J. A. Amick, *J. Electrochem. Soc.* **113,** 724 (1966).
5. Additional details have been presented in talks by A. E. Blakeslee at the Electrochemical Society Meeting, Los Angeles, May 11–15, 1970, and at the International Symposium on GaAs and Related Compounds, Aachen, Germany, Oct. 5–7, 1970. These papers will appear in the *Journal of the Electrochemical Society* and the *Symposium Proceedings,* respectively.

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