The route towards the implementation of graphene in “real world” microelectronic applications exploiting the exceptional graphene properties comprises the development of scalable deposition techniques. Chemical vapor deposition is deemed as one of the most promising techniques to achieve graphene crystals. At now, two major hurdles in the advancement towards a CMOS-compatible, graphene-based microelectronic platform are present: the achievement of metal-free graphene and the further improvements in the graphene quality. The growth of graphene directly on Ge or Ge/Si substrates (in particular on the technology relevant (001) surface orientation) recently demonstrated could be a breakthrough toward CMOS compatibility, since no catalytic metal surfaces are required. We will present the results of our study of the CVD graphene growth process on Ge(001) substrate. We investigated the kinetic of the growth by a combined use of µ-Raman, x-ray photoelectron spectroscopies, scanning electron and scanning tunneling microscopies. We were able to establish different growth regimes—yielding to graphene nanoribbons, graphene deposited in a layer by layer regime and graphene multilayer—by simply varying the carbon precursor flow. In the layer-by-layer growth regime, reliable and well controlled growth of graphene monolayer with quality exceeding the state of the art for graphene synthesis on Ge is obtained. We also investigated the early stage of CVD graphene synthesis which deeply influences the resulting graphene quality. We identified the carbon precursor phase to graphene nucleation, made of C aggregates with different size, shape and local ordering. The C precursor phase evolves gradually towards graphene domains through a crystallization process that ultimately results in the formation of a uniform single layer graphene.